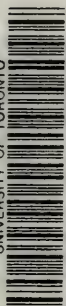


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AN INTRODUCTION
TO
CHEMICAL CRYSTALLOGRAPHY
ANDREAS FOCK

HENRY FROWDE, M.A.
PUBLISHER TO THE UNIVERSITY OF OXFORD



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AN INTRODUCTION
TO
CHEMICAL CRYSTALLOGRAPHY

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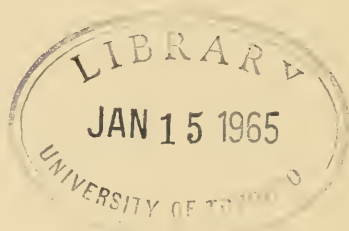
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P R E F A C E

IN 1888 Dr. Fock published the little treatise entitled *Einleitung in die chemische Krystallographie*, in which he summarised the results of recent investigation and the views deduced from them on the subject of crystal-growth in its relation to some chemical problems: and in the present small volume this admirable summary has been enlarged by additions necessitated by the advances made in this important subject since 1888. The form of brief chapters into which the discussion is thrown, chapters each devoted to the exposition of a single idea, invests Dr. Fock's little book with a singularly readable character, and its translation by Mr. Pope will have brought it within the reach of University and other students, to the majority of whom its original German dress would present considerable, if not insuperable, difficulties.

The broad divisions of the subject fall under the following heads:—

(1) Crystal growth, in the discussion of which due importance is given to the extensive and laborious investigations of Lehmann.

(2) The laws controlling the equilibrium between the elements of a solution at different pressures and temperatures; those elements, when we consider the pressure as constant, being the solution and crystal-solid, the former of which may be considered as consisting of the solvent and what for lack of a much-needed term I may call the *solute* (namely the substance or substances dissolved).

(3) Salts containing water of crystallization, double salts, and isomorphous substances are treated each in its turn; and the final chapters deal (4) with both physically isomeric and isogonous substances and with the crystallographic changes attending the substitution of one radicle or element by another.

A freshness of interest is imparted to each of the larger subjects by a concise but sufficient survey of the historical growth of the ideas involved in them: for frequently whilst tracking the steps by which a scientific idea has become confirmed or corrected by the progress of collateral investigations during more than one generation of workers, we best learn to appreciate the grounds on which contemporary theories rest.

Perhaps the most important of the chapters in this edition of the *Einleitung*, are those which deal with the subjects I have grouped under the third division—namely salts containing water of crystallization; double salts; mixed crystals and isomorphous substances.

It is unnecessary to recapitulate the conclusions logically drawn under these several heads; the methods adopted for treating them being in many respects

analogous throughout and amply discussed in the pages that deal with them.

These methods are founded on the laws controlling the equilibrium of a solution, as between the solvent, the solute or solutes, and the undissolved crystal or crystals under varying conditions of temperature, and, where not in open vessels, of pressure, and involve a study of the accompanying variations in 'osmotic' pressure. The analogies between the laws of Boyle and Gay Lussac, and (as shown by van't Hoff) of Avogadro regulating gases and those governing dilute solutions, are extended to corresponding analogies between saturated solutions and saturated vapours; we have further the fertile suggestion on the part of van't Hoff, that isomorphous mixtures are, at all events in certain cases, solid solutions of one substance in another. By a consideration of the laws of equilibrium in a solution under varying conditions defined by the phase-rules which have been deduced from thermodynamical principles by Willard Gibbs, Dr. Fock in his seventh chapter gives a lucid explanation of the well-known phenomena presented in crystallization from supersaturated solutions, as exemplified by the separation of sodium sulphate and its various hydrates from solution: and in his eighth chapter he deals in a similar way with the formerly perplexing question of double salts. But in the eighteenth, the newest and most important chapter in his treatise, he has discussed at some length the question of isomorphous mixtures in the light of the powerful methods applied to the subject by Bakhuis Roozeboom, who, accepting van't Hoff's view of solid solutions, and taking the composition of the solution (i.e. the molecular

proportion of the different solutes) as bearing a direct relation to the composition of the crystallized salts, determines the conditions of equilibrium between the mixed crystals and the solution, under constant conditions of temperature and pressure.

He in fact, with the aid of the phase rules of Willard Gibbs, defines the conditions of equilibrium in the case of crystallized mixed substances in contact with their solution.

A crucial test perhaps of van't Hoff's bold hypothesis regarding solid solutions will be attained in determining whether any sound evidence of a partial pressure corresponding to osmotic pressure can be brought forward in cases analogous to those of dilute solutions where a small amount of one isomorphous substance is, to use the language of the hypothesis, dissolved in a large amount of another. The electrolytic transference of sodium and of lithium through glass may be quoted as collateral evidence, indicating that a pressure of this nature may operate in solids; and the passage of carbon into steel, familiar in the old cementation process, may possibly be interpreted as the result of such a pressure. And if there be a true analogy between such solid solutions and liquid solutions in regard to osmotic or internal pressure, and if there be a constant relation independent of the concentration between the solute in the liquid and the solute in the corresponding solid solution, the methods that are available for determining molecular magnitudes in the former should be applicable also to the extension of our knowledge of the molecular magnitudes of the solid substance held in solution in an isomorphous mixture. Nernst

has already grappled with this question, and doubtless it is one to which investigation will now be directed by the application in other ways of the methods adopted by Roozeboom.

An important application of the principle involved has recently been made by Küster, who has determined the molecular weight of a liquid dissolved in a solid, and already claims for his investigations that they constitute a first and striking confirmation of Nernst's 'Law of Distribution,' of a solute between two solvents, one of which is solid.

The term solid solution was in the first place applied by van't Hoff to the case of an isomorphous mixture; it would seem, however, from a study of the cryoscopic method of determining molecular weights made by Ferratini and Garelli, that the term may require widening so as to include mixtures of substances, which though not isomorphous, are chemically allied. Mr. Pope's translation includes references to the recent work of Muthmann and of Tutton, and in fact the treatise brings before the student the particular subjects that are discussed, in the light in which they stand in the scientific thought of to-day.

It may be expected that this treatise may serve a further purpose, that namely of drawing the minds of the chemical students in English Universities and Colleges to the consideration of the important light thrown on their work and on their views of Chemistry by associating with these the study of the dynamical laws that underlie the processes in which they deal, and of Crystallography which is the key to their interpretation. Does the

chemist, who perhaps prides himself on calling into existence crystallized substances heretofore unknown, consider his work only half done when he is unable to determine the symmetry and the constants, crystallographic and physical, which characterise his production, and are as much a part of its nature as its composition and chemical relationships?

N. S. M.

November 18, 1894.

TRANSLATOR'S PREFACE

IN preparing the present edition of Dr. Fock's little work I have been actuated by two motives : firstly, by the desire to provide an elementary text-book dealing with the chemical bearings of crystallography for the use of students at the Central Technical College ; and, secondly, by the desire to make clear to English chemists the great importance of a knowledge of crystallography to their science.

During the past few years it has become very generally recognized that most important advances in crystallography are to be expected from the chemical side ; our knowledge of the physical and geometrical properties of crystals is now very complete, but their relations to chemical constitution and composition are as yet but little known. Yet, on the other hand, the study of these very characters by mathematicians and mineralogists has yielded results which intimately affect some of the highest problems in physical and organic chemistry. This fact is only one amongst many which render it necessary that an important place in the chemist's education should be assigned to crystallography ; thus the pressing need

of some physical property, the determination of which should supplement that of the melting-point in the characterization of new compounds would disappear if it were customary amongst chemists to examine the behaviour of such substances in the polarizing microscope. An examination of this kind can be made almost as rapidly as a melting-point determination, and would afford, in most cases, an infallible test of the identity or non-identity of two substances; such a test is certainly not to be found in the melting-point, because of the small range of expression of this property and its liability to be affected by slight impurity.

In the endeavour to make the book a truthful statement of the position held to-day by crystallography as a branch of physical chemistry, Dr. Fock has considerably modified and enlarged the original German edition, so as to include much recent work of importance; and with the author's sanction, I have also made a number of additions.

My friend, Mr. H. A. Miers, of the Natural History Museum, has made a careful revision of both manuscript and proofs; I would wish to add that the obligation which this very considerable service imposes on me is small in comparison with my indebtedness for his untiring patience and generous assistance during the years which I have spent as his pupil.

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CONTENTS



	CHAPTER I.	PAGE
INTRODUCTION		I
	CHAPTER II.	
THE NATURE OF CRYSTALS		7
	CHAPTER III.	
THE PHYSICAL LAWS GOVERNING CRYSTALLIZATION		15 6
	CHAPTER IV.	
FUSION AND SOLIDIFICATION		19
	CHAPTER V.	
SUBLIMATION		22
	CHAPTER VI.	
SOLUTION AND SEPARATION		24
	CHAPTER VII.	
WATER OF CRYSTALLIZATION		29
	CHAPTER VIII.	
DOUBLE SALTS		36
	CHAPTER IX.	
ORIGIN AND GROWTH OF CRYSTALS		42 4
	CHAPTER X.	
FORMATION OF CRYSTALS. CRYSTALLITES		45 .
	CHAPTER XI.	
THE PROCESS OF CRYSTALLINE GROWTH		50 .
	CHAPTER XII.	
STRUCTURAL ANOMALIES		58

CHAPTER XIII.		PAGE
THE OCCURRENCE OF DIFFERENT SIMPLE CRYSTALLINE FORMS	.	64
CHAPTER XIV.		
GENERAL RULES FOR THE ARTIFICIAL PREPARATION OF CRYSTALS	.	68
CHAPTER XV.		
SPECIAL METHODS OF PREPARING CRYSTALS	72
CHAPTER XVI.		
HISTORICAL SKETCH OF ISOMORPHISM	82
CHAPTER XVII.		
THE GEOMETRICAL AND PHYSICAL PROPERTIES OF ISOMORPHOUS SUBSTANCES	89
CHAPTER XVIII.		
THE CHEMICAL PROPERTIES OF ISOMORPHOUS SUBSTANCES	106
CHAPTER XIX.		
THE PROPERTIES OF MIXED CRYSTALS	133
CHAPTER XX.		
GENERAL CONCLUSIONS RESPECTING ISOMORPHISM	140
CHAPTER XXI.		
HISTORICAL SKETCH OF PHYSICAL ISOMERISM	143
CHAPTER XXII.		
THE PROPERTIES OF PHYSICAL ISOMERIDES	147
CHAPTER XXIII.		
THE NATURE OF PHYSICAL ISOMERISM	161
CHAPTER XXIV.		
HISTORICAL SKETCH OF ISOGONISM	167
CHAPTER XXV.		
MORPHOTROPY	173
<hr/>		
INDEX TO AUTHORS' NAMES	185
INDEX TO SUBJECTS	187

CHEMICAL CRYSTALLOGRAPHY

CHAPTER I.

INTRODUCTION.

THE ancients were well aware that certain mineral substances occur in definite regular forms which are bounded by plane surfaces, and are frequently distinguished by the possession of great lustre. Rock crystal was the most important of such substances known to them, and the name of this widely disseminated mineral is derived from the similarity which it bears to ice as regards transparency and clearness. The name crystal ultimately became a generic one for all such substances.

The ancients, as well as the investigators of the Middle Ages, were completely ignorant of the origin or mode of formation of crystalline bodies. Even during the eighteenth century the opinion prevailed that crystals, like animals and plants, owe their formation to the operation of organic forces. The ignorance of the earlier workers in this respect seems the more astonishing, when it is considered that the observation of the artificial growth of crystals must be as old as the use of common salt, and that the Arabian Alchemist Geber, about the middle of the eighth century of our era, obtained various salts in a crystalline form, and even recommended crystallization as a means of purifying substances.

The external regular form of crystals was supposed to be purely an accidental property, having no connexion with their composition. The process by which this opinion was arrived at can be readily understood, since certain crystals, whilst obviously consisting of the same substance, are so different in outward appearance owing to unequal development of the faces, that not the least similarity can be traced between them by mere inspection. In the sixteenth century Gessner (1568) was so misled by these circumstances as to assert that the individuals of one and the same crystalline substance are not only of different sizes, but that the mutual inclinations of the faces are different and the whole external forms dissimilar. This view was generally accepted even in the second half of the eighteenth century, although Nicolaus Steno (d. 1686) had long before (1669) noted the equality of the angles on different specimens of rock crystal, and Guglielmini (d. 1710) had established the constancy of crystal angles as a general law. The latter worker further occupied himself with speculations upon the structure of crystals, but his views attracted little attention; he was followed by Boyle and Lemery, who were the principal students of crystallography in the seventeenth century.

At the beginning of the sixteenth century Cæsalpinus (d. 1603) observed that saltpetre, alum, sugar, and the vitriols, always separate from their solutions in the same characteristic forms: being led astray, however, by the generally accepted idea that crystals are the products of some organic process, this author did not draw the obvious deduction from his observations, i.e., that the crystalline form must be considered as a characteristic property of the substance.

The work of Boyle (d. 1691) tended in much the same direction as that of his predecessor Guglielmini. He made

observations on the phenomena attending crystallization, and showed that the rapidity with which the solution cools is of special influence upon the habit of the separating crystals; he observed also that the forms assumed by various substances differ among themselves in a regular and definite manner. He was, however, just as far from concluding that the same salt always possesses the same crystalline form, as were his predecessors.

Lemery paid special attention to the differences between the crystalline forms deposited from solutions of an alkali in different acids, &c. His work was of a very crude nature and was practically limited to questions of size and thickness. Thus, he observed that the crystals obtained from a solution of an alkali in acetic acid are more acute in form than those separating from a nitric acid solution, and these latter, in turn, appear yet more sharply pointed than those deposited by a solution of an alkali in sulphuric acid. He expected to find an explanation of these phenomena in the nature of the acid employed, or, as he expressed it, in the 'thickness' of the acid particles. A little later, Homberg endeavoured to explain the differences between the crystalline forms of various salts, but arrived at no more precise conceptions than Lemery.

One of the chief obstacles to the more rapid progress of this branch of science, in addition to the extremely incomplete knowledge of crystalline forms, was the condition of chemistry at that date. Towards the middle of the last century, however, as the development of chemistry proceeded more rapidly, and the description of individual crystalline forms assumed a more scientific character, it became partly recognized that differences in the chemical composition of substances are attended by a change in the crystalline form; in general, however, it was supposed that crystals of one and the same substance differ, not only in

the size of the faces, but also in the magnitude of the angles.

Towards the end of the last century our knowledge of crystals began to increase rapidly. Bergmann (d. 1784) and Gahn discovered the cleavage of crystals. Certainly, this property had already been observed in calcite, but it was regarded merely as a general property of the material, and not as having any connexion with the crystalline form. Bergmann was led by his discoveries to speculations upon the structure of crystals, such as had previously attracted Guglielmini; these theoretical considerations, however, like those of his predecessor, were quite without influence upon the development of the science.

The careful comparative studies of Romé de l'Isle and his contemporary, Werner, upon the nature of crystalline forms, next merit notice. Werner (d. 1817) sought more particularly to discover a relation between the forms of different crystals of the same substance. For this purpose he endeavoured to derive new forms by truncating, bevelling and replacing certain fundamental forms; he chose as these fundamental forms, the cube, the pyramid, the prism, the plate, and a lenticular figure. His work, however, led to little result, owing principally to his assumption that one and the same substance could possess different fundamental forms.

Romé de l'Isle (d. 1790) also endeavoured to discover relations between the various shapes of crystals. Further, he not only described the various forms observed on natural crystals, but constructed models of them. Whilst Linnæus (d. 1778) was acquainted with only 40 different crystalline forms, de l'Isle in his first investigation described 110, and ultimately determined and modelled no less than 500 such forms. To the circumstance that de l'Isle not only described his crystals, but constructed

models of them, we are indebted for one of the most important crystallographic inventions. Up to that time, measurements of crystal angles had been made by measuring the edges and diagonals of the faces with compasses, and from these lengths calculating, first, the plane angle, and, subsequently, the solid angle. In order that the models might be the more readily constructed, de l'Isle's assistant, Carangeot, devised the so-called contact goniometer; this instrument proved of the greatest value in the further development of crystallography. Steno had, many years before, observed the constancy of the angles on rock crystal; by the use of the goniometer de l'Isle was able to assert the same of other substances, and place the general law enunciated by Guglielmini on a firm basis. The valuable work of de l'Isle has, unfortunately, found but slight recognition; partly because small attention was paid to such kinds of research at that time, and partly because, a little later, the crystallographic studies of Haüy aroused far greater interest, and so obscured the work of his immediate forerunner.

Réné Just Haüy must be recognized as the real father of crystallography; it was reserved for him to establish the science upon the firm foundations laid by previous workers, more especially by de l'Isle. Haüy's influence upon crystallography dates from about 1782, when he established the general character of different kinds of crystalline series from a study of the laws of symmetry. He showed, for example, that the series derived from the cube could only include certain regular forms, such as the octahedron and dodecahedron. He sought to refer all crystalline forms which possess the same symmetry to one simple fundamental form. The great difficulty presented by this problem, especially with the limited means at Haüy's disposal, will be appreciated when we consider

the enormous number of forms exhibited by calcite. Even now, the expert sometimes finds it no easy matter to recognize the constant crystalline form of this mineral amongst the numerous variations in shape which it presents. Haüy, however, followed up his work with great perseverance, and was at length able to refer all the different forms assumed by a crystalline substance to one simple fundamental form; he was thus led to discover the general law now universally known as the law of rational indices to which all crystals without exception are subject.

Haüy's penetration further enabled him to recognize in the magnitudes of the crystalline angles, as well as in the general crystalline form, an important means of identification; consequently, he saw in crystallography a most powerful instrument for determining crystalline minerals. In connexion with this latter object he interested himself considerably in chemical research, wishing to verify by analysis the crystallographic differences observed between minerals. In the majority of cases this attempt proved successful, and he therefore concluded that, leaving the cubic system out of consideration, every definite crystalline chemical compound can be referred to a characteristic fundamental form. In other words, he showed that differences in chemical composition find expression in the crystalline form, and that two different substances do not crystallize in the same form.

These views soon found universal acceptance, and at the present time form the basis of chemical crystallography. The exceptions exhibited in this respect by certain substances do not invalidate the law, as they find a natural explanation in the close chemical relationship existing between such compounds.

CHAPTER II.

THE NATURE OF CRYSTALS.

IN considering the problems of chemical crystallography it is essential to possess the clearest and most correct conceptions of the character and nature of crystals. For this purpose an exact definition of a crystal must first be given, which shall harmonize both with the geometrical and physical properties of crystals and also with what is known of crystalline structure.

As is well known, the geometrical properties or the external regular shapes of crystals are governed by the general law which asserts that when the positions of four independent faces are fixed, the position of any other face is not an arbitrary one, but must fulfil certain definite conditions. These conditions may be formulated in terms of 'Indices,' of 'Zones,' or of 'Anharmonic ratios'; thus, the fundamental law is variously termed the law of rational indices, the law of zones, or the law of rational anharmonic ratios. These three laws in reality express precisely the same fact. The fundamental law, however, does not merely express the relative positions of the separate faces, but also implies the co-existence of certain faces constituting a 'simple' crystalline form.

So-called crystalline symmetry is, in reality, merely a consequence of the law of rational indices. This fact was only slowly recognized, and was first clearly and completely expressed in 1866 by Viktor von Lang in his

Lehrbuch der Krystallographie. By the application of purely mathematical methods to the fundamental principles of crystallography, this author was able to show what kinds of symmetry are, and what are not, possible amongst crystals. There is, in this question of symmetry, a complete accord between theory and experience. All the properties resulting from symmetry recognized as theoretically possible, actually occur in practice, and conversely no such properties have been observed which could not have been anticipated by theory.

The physical properties of a crystal are the same in parallel directions, but are, as a rule, different in different directions; they thus differ from the corresponding properties of homogeneous amorphous bodies which are the same in all directions. In a crystalline medium the cohesion and elasticity in general vary with the direction; the other properties, however, do not all conform to this rule. The physical properties are absolutely and alone dependent on the direction, because at no point in the interior of the crystal are the properties different from those at any other point; there is no *singular* point. The properties of pieces cut from various parts of an individual crystal are always the same.

A noteworthy relation which exists between the geometrical and physical properties of crystals is that every plane of geometrical symmetry is likewise one of physical symmetry: the converse of this, however, is not generally true; the physical properties may hence be divided into two groups according as the geometrical and physical symmetry is, or is not, of the same order. To the first class belong cohesion, elasticity, and the pyroelectrical properties; to the second, the optical, thermal, magnetic, and some of the electrical properties. The latter are of a higher order of symmetry than the former.

A crystal may thus be defined, on the basis of all its properties, in somewhat the following terms: *A crystal is a homogeneous solid body of definite chemical composition, whose physical properties are the same in parallel directions, but are generally different in directions which are not parallel.* The outward sign of a crystal is its regular geometrical form; this, however, is only perfect if the development has proceeded undisturbed, and is by no means an essential feature of the crystal. The external form may be destroyed, and yet the fragments will not cease to be crystals; on the other hand, the most perfect crystal model is not a crystal, lacking, as it does, the characteristic internal physical properties.

The best explanation of the peculiar character of a crystal is to be found in the assumption that its ultimate particles are arranged in a regular manner, whilst in an amorphous body there is no such regularity. By the structure of crystals, therefore, is understood the regular arrangement of the molecules.

Speculations on crystalline structure were rife long before the development of the fundamental laws of crystallography. Thus Guglielmini was of opinion that all crystals consist of minute fundamental figures (the cube, octahedron, and the hexagonal and oblique prisms), built up in a definite and regular manner, and held together by magnetic forces. Before this, however, Robert Hooke (1667) had sought to explain the crystalline form of alum by supposing it built up from cubes of equal sizes.

The speculations of Huygens (d. 1695) attracted more attention than those of Guglielmini, and resulted from their author's researches on calcite. Huygens considered that a crystal, such as calcite, is built up in a regular way from small invisible particles, to which he assigned an ellipsoidal form, suggested in this instance by the ascertained form of the optical wave-surface. The work of Bergmann on this

subject next deserves mention: Gahn had observed that all calcite crystals cleave into rhombohedra; Bergmann therefore concluded that some close connexion must exist between the cleavage figure and the different crystalline forms; accordingly, he endeavoured to derive the hexagonal prism and the scalenohedron from different arrangements of cleavage rhombohedra. Haüy was, however, the first to grasp the general connexion between the cleavage fragments and the crystalline form; he succeeded not only in founding a theory of the molecular structure of crystals upon the phenomenon of cleavage, but also in deducing from it the fundamental laws of crystallography.

Haüy considered the smallest particles (*molécules intégrantes*) of a crystal to be plane-sided polyhedra, by the aggregation of which a crystal nucleus of the same shape as the principal cleavage form is produced. In many cases this nucleus is supposed identical in form with the integrating molecule; where this is not so, the reason is to be found in the nature of the cleavage. Thus, tourmaline cleaves both on the rhombohedron and prism forms, the latter cleavage being imperfect; a cleavage rhombohedron can thus be divided into six acute tetrahedra. These last, therefore, Haüy considered as the integrating molecules, and took the rhombohedron for the nucleal or fundamental form; such a nucleus (*forme primitive*) constitutes the fundamental form from which all others may be derived. The same conclusion is arrived at from a consideration of the process of crystallization; the growth of a crystal occurs in such a way that the new material is deposited in layers on the faces of the primitive form. In his mathematical theory Haüy supposed that the elements (*molécules soustractives*) of these layers are always parallelepipeda. The subtractive molecules, therefore, may be so far identified with the integrating mole-

cules in that both are parallelepipeda. The agreement is, however, not complete; for, in the special case of a substance having octahedral cleavage, the integrating particles cannot be placed side by side without gaps intervening; the assumption must, therefore, be made that the subtractive molecules are of a complex nature.

In order to explain the occurrence of the various derived forms, it is further assumed that the successive layers deposited during the building up of the crystal become gradually smaller and smaller in area, each layer being less by several subtractive molecules than the preceding one. In this way a pyramidal growth is obtained, whose precise form differs according as the molecules recede along a line parallel to the edges of the fundamental form, parallel to diagonals of the faces, or lastly, parallel to certain intermediate directions.

In accordance with the above theory Haüy explained morphological features of this kind by a double process; the nucleal form of the substance considered had first to be determined, and then the complete crystalline form had to be referred back to this nucleus. The question whether the subtractive molecules were identical with the integrating molecules or were merely constructed from them seemed to Haüy of but little importance.

A critical consideration of Haüy's theory shows it to be by no means free from defect; many substances occur which possess no parallelepipedal cleavage or have it but imperfectly developed. Certain contradictions are also evident; as, for example, that octahedral molecules cannot be placed in juxtaposition without the intervention of vacant spaces. The latter objection was, however, eluded by Seeber¹, who substituted smaller spherical molecules in place of Haüy's contiguous polyhedral units; this at the same time

¹ *Gilb. Ann. d. Phys.* 76, 229, 1824.

provided a possible explanation of the expansion of crystals. Later on, one of Haüy's pupils, Delafosse (1843), independently and in a similar manner devised a theory in which material points took the place of Haüy's molecules.

Wollaston (1813) endeavoured to remove certain contradictions connected with the supposed regular form of the integrating molecules. For this purpose he assigned to the latter spherical and ellipsoidal shapes, and assumed them to preserve their regular arrangement in virtue of mutual attractive forces which bring them as closely as possible together. The opinion held by James Dana (1836) was developed from the foregoing; in place of Haüy's subtractive molecules he considered their inscribed ellipsoids, and also identified the latter with the integrating molecules.

All these developments of Haüy's theory are concerned merely with the shape of the crystalline elements; the latter were always supposed to have a parallel or net-like arrangement. This arrangement is the same as is peculiar to the so-called 'space-lattices,' and was not considered worthy of special study.

Frankenheim¹, was the first to investigate the nature of the possible space-lattices and showed that they must possess the same symmetrical properties as crystals themselves. He found that fifteen different space-lattices are possible, and then, having deduced from the cleavage and general habit of crystals that fifteen fundamental forms of crystals are possible, he showed that these latter in many respects correspond with the lattices. Frankenheim's views are not in all respects correct, but they were of value in opening up new ground.

Some time afterwards Bravais² (1850) showed that two of the fifteen networks described by Frankenheim are identical

¹ *Die Lehre von der Kohäsion*, Breslau, 1833.

² *Études cristallographiques*, Paris, 1866.

and also that the fourteen which remain can be divided into seven groups, within each of which the members are characterized by the same symmetry. These groups agree in general with the seven known crystalline systems, considering the rhombohedral forms to constitute a system distinct from the hexagonal. The agreement is, however, not complete; the fourteen space-lattices represent the holohedral forms alone and the properties of hemihedral crystals are not considered. In order to supply the omission of the structure of hemihedral crystals in the theory of space-lattices, Bravais then introduced a supplementary hypothesis according to which the hemihedral character of a substance is conditioned by the nature and form of the crystalline elements; the holohedral and hemihedral forms (say of cubic crystals) may thus possess the same net-like structure, but must consist of crystalline elements which differ in their symmetry.

Although this extension of the original hypothesis cannot be really regarded as inadmissible, Sohncke¹ considered that it was of a somewhat arbitrary nature; he therefore treated the problem from a more general point of view. Starting from the same fundamental principle—that, in an indefinitely extended crystalline system of points, the distribution of the points round each point is the same—he endeavoured to deduce all the kinds of structure possible. The conclusion at which he arrived was as follows: if it be admitted that, in this distribution of points, the individual molecules are arranged parallel to one another, then the only possible form of structure is a reticular one. If this be not admitted, it can be shown, as had already been done independently by C. Wiener², that other structural forms are conceivable.

¹ *Entwicklung einer Theorie der Krystallstruktur*, Leipzig, 1879.

² *Grundzüge d. Weltordnung*, 2nd ed., 1869, vol. i.

From his more general point of view, Sohncke¹ was then able, with the aid of some purely mathematical reasoning of Camille Jordan, to demonstrate that sixty-five such regular, infinite point-systems are possible. Further, he showed that these sixty-five systems may be grouped in accordance with the symmetry of the various known crystalline systems.

The forms of structure described by Bravais can thus only be regarded as special cases from amongst a number of systems which explain the symmetry of hemihedral and tetartohedral, as well as of holohedral crystals.

Further, point-systems of this kind explain clearly the optical activity of many crystalline substances as well as the existence of so-called 'limiting' forms. The theory may hence be considered as well founded; it will naturally attain to a higher degree of probability when the individual point-systems are identified with known crystalline substances, and the properties of the latter, together with their relations to kindred bodies, are clearly defined. At present this has only been attempted for a few individual cases, and more particularly for quartz, which was studied by Sohncke himself. More recently Sohncke's method has been extended by Federow, Schönflies, Curie, and Barlow, and in a different manner by Sohncke himself, with the result that the number of possible crystalline structures has been largely increased and includes all the varieties of crystalline symmetry, both holohedral and hemihedral.

¹ *Zeitsch. f. Kryst.* xiii. 218.

CHAPTER III.

THE PHYSICAL LAWS GOVERNING CRYSTALLIZATION.

UNTIL the middle of the last century it was generally supposed that crystals, like animals and plants, owe their origin to the operation of organic forces. The investigations of Bergmann and Haüy, which led to definite conceptions of crystalline structure, caused a change in the prevailing opinion, and resulted in the formulation of two views respecting the growth of crystals. By some it was supposed that the crystalline elements are built up in a regular manner owing to their polyhedral forms and to the attractive forces operating between them; others saw in the process of crystallization only the action of electrical and magnetic forces.

Beudant (compare p. 82) was one of the first to apply himself energetically to the study of the process of crystallization; his work aimed at the discovery of the initial cause which leads matter to assume these varied and characteristic forms. To attain this end he studied the influence of the pressure and moisture of the atmosphere, the concentration, mass, and temperature of the solution, and the shape of the containing vessel upon the form of the crystals deposited; further, he investigated the action of electricity and magnetism upon crystallization. His work led to no important result; he merely found that changes in the above-mentioned conditions result only in a slower or more rapid growth, or in a larger or smaller development of

the deposited crystals, and that such changes effect no alteration in the form of the resulting crystals. A definite change in the form of the crystals could, however, be caused by the addition of certain chemical reagents to the solution. Thus, he observed that alum is deposited from its solution in cubes, when purified from all free acid by heating with an insoluble carbonate, and that common salt separates from urine in octahedra.

Le Blanc, von Grotthus, and Gay-Lussac, together with numerous other workers, succeeded Beudant in the study of this subject, and the opinion was often expressed in the literature of the period that crystallization is an electrical or magnetic process. This view received substantial support from the study of pyroelectrical phenomena and also from the fact that certain crystals, such as those of arsenious anhydride, emit light at the moment of separating from solution. All attempts, however, to arrive at a more perfect conception of the process of crystallization in this way have been futile ; such work, consequently, hardly merits more special mention.

Molecular forces are the active cause of crystallization, determining, as they do, a certain attraction between the crystalline elements. This statement, although vague, is at present the most definite that can be safely made ; though many interesting facts which indicate that a relation exists between the environment of a crystal and its habit have been discovered by von Hauer and others.

The property of assuming a crystalline form is apparently not common to all substances ; a large number of compounds are known which have not yet been obtained in the crystalline state. Among these may be enumerated albumen, tannic acid, the gums, &c. ; these substances are known as *colloids* in contradistinction to *crystalloids* or crystallizable compounds. There are, however, other ways

of distinguishing between colloids and crystalloids; the former, for example, possess a very slight power of diffusion, and the presence of dissolved colloids affects the boiling or freezing point of a solvent but slightly, thus indicating that they have very high molecular weights. Although colloids seem to possess no power of crystallizing, a final distinction cannot yet be drawn, for it may be that it is only a matter of difficulty, and not of impossibility, to establish the conditions necessary to the crystallization of such substances¹.

The principal condition for obtaining a substance in a crystalline form is fulfilled if it be possible to change it from the gaseous or liquid into the solid condition. Many substances are known which under ordinary circumstances exist in the gaseous state, and whose conversion into the solid state may be effected in accordance with known physical laws simply by lowering the temperature, or by the combined effect of cooling and increased pressure. Conversely, if a substance is already solid, it must, in general, be converted into the fluid state before crystallization can occur; two ways of accomplishing this exist.

The first consists in heating the substance till it melts or volatilizes; on cooling, the substance is obtained again in the solid state. Many substances may thus be caused to crystallize by condensation of the vapour or by slow solidification of the molten mass. Ammonium chloride crystallizes as it solidifies from the gaseous state; sulphur, iodine, camphor and benzoic acid crystallize as they solidify either from the gaseous or liquid state.

The second method of obtaining a substance in the crystalline form consists in causing it to separate from solution; water is the usual solvent employed, only a few other liquids, such as alcohol, ether, carbon bisulphide, and

¹ Schimper, *Zeitsch. f. Kryst.* v. 131.

petroleum, having any practical importance in this respect. The employment of other fluids, such as gases, or the molten substance itself, as solvents for crystallization, has received but little attention. From a physical point of view, three methods for the preparation of crystals may be distinguished, i.e., solidification from the gaseous, molten, or dissolved state (see, however, p. 80).

When it is considered that the process of crystallization is in general a reversible one, it is evident that a knowledge of the phenomena attending the conversion of solid or crystalline substances into the gaseous, liquid, and dissolved states, is all-important to a correct understanding of the process of crystallization. The phenomena accompanying sublimation and fusion will therefore be briefly discussed, whilst the process of solution, possessing, as it does, much more importance in connexion with the artificial preparation of crystals, will be treated at greater length.

CHAPTER IV.

FUSION AND SOLIDIFICATION.

THE temperature at which a substance passes from the solid to the liquid state is a perfectly definite one ; it is termed the *melting point* and is constant for the same compound. The melting point of a substance is identical with its *freezing point*, i.e., the temperature at which the liquid substance solidifies. This temperature being constant and characteristic for chemically simple substances, is much employed for purposes of identification. The melting point is only affected by the superincumbent pressure ; the alteration in the point of fusion caused by a change in atmospheric pressure is a definite one, but is so insignificant that for all ordinary purposes it may be ignored. Thus, according to Thomson, the melting point of ice is lowered by only 0.00733° per atmosphere of pressure added.

The molecular structure of a substance has considerable influence upon its point of fusion. Thus a body has two different melting points according to its condition, whether amorphous or crystalline ; and in those cases where a substance assumes two different crystalline forms, each variety has its specific melting point. Certainly, in most cases the various modifications differ slightly in this respect, but differences of several degrees are frequently observed. For this reason, the value of melting point determinations as a means of recognition and identification of chemical products has fallen considerably of late years.

The conversion of a solid body into the liquid or gaseous state is always accompanied by two phenomena which are closely related to one another, i.e., a change in volume and a transference of heat. The alteration in volume observed on melting differs not only in magnitude for different bodies but also in sign; the change is, however, constant both in sign and magnitude for every chemically homogeneous substance. Most substances increase in volume on changing from the solid to the liquid state; amongst the few substances which show the opposite behaviour, i.e., which decrease in volume on melting, are water and a few metals, such as iron, copper, antimony and bismuth. It is easy to decide *a priori* whether the melting point of a substance will be raised or lowered by change of external pressure. The direction of the change in melting point evidently depends upon the direction of this alteration in volume; if a substance increases in volume on melting, the melting point rises on increasing the pressure, and *vice versa*.

The transference of heat observed on melting, like the change in volume, is of constant magnitude; the former change, however, only proceeds in one direction. Heat is always absorbed, and never liberated, during fusion. This fact is fully explained by our current ideas concerning the nature of heat; heat consists in the motion of the molecules of bodies, and work and heat are interconvertible. When a substance is converted from the solid to the fluid state, a certain definite amount of work has to be done in order to overcome the external pressure and the attraction between the particles of the body, both of which causes tend to prevent increase in volume. In melting, then, two kinds of resistance have to be overcome—an internal and an external. The external resistance exists only for those substances which increase in volume on melting; with

substances which decrease in volume on liquefaction, the external pressure assists the process of fusion. The internal resistance to fusion which has to be overcome is always so great as to render the effect of the external pressure insignificant. Heat is never liberated on melting, but must always be put into the body in order to lessen the molecular attraction and so bring about liquefaction. On solidification the reverse change naturally occurs, the heat taken up in melting being again set free. This liberation of heat retards the solidification and so establishes more favourable conditions for that regular arrangement of the particles of the substance which results in the formation of crystals.

CHAPTER V.

SUBLIMATION.

By sublimation is understood the process by which a substance passes directly from the solid to the gaseous state on the application of heat, and subsequently returns to the solid state on cooling. The term is also applied to those cases in which liquefaction occurs during the heating but not during cooling, the vapour passing directly into the solid state ; such cases are frequently met with amongst those substances whose melting and boiling points lie near together. This condition, however, is but seldom fulfilled, the melting and boiling points of a substance generally lying far apart. A clearer conception of the process will be obtained when it is considered that both melting and boiling points vary with the external atmospheric pressure ; the latter temperature changes rapidly and the former very slowly. In some few cases sublimation occurs under ordinary barometric pressure, and by decreasing the atmospheric pressure it is very often possible to effect the direct conversion of a solid body into the gaseous state. Naturally no definite change of volume can here be spoken of, as gases have no constant volume. The heat absorbed in sublimation is the sum of the heats of liquefaction and of vaporization.

The gaseous condition of certain substances, considered in its relation to the crystalline state, allows of some important

observations¹. As is well known, sulphur belongs to that class of elements of which the members are known in all three states of aggregation; under standard pressure this element boils at 417° and freezes at about 120° . It has been found that sulphur vapour at a temperature of $1,000^{\circ}$ is composed of molecules—chemical molecules—formed by the combination of two atoms. On cooling the gas to 800° , vapour density determinations show that condensation is beginning to occur with the formation of larger molecules; at 500° the gas consists entirely of physical molecules—that is to say, of freely moving particles each consisting of six atoms. The condensation of three chemical molecules to form one physical molecule is naturally accompanied by an evolution of heat, as the chemical molecules give up a great part of their independent motion and the velocity of the resulting large molecules becomes smaller in proportion to their size. In this case, therefore, as in all others, change of state of aggregation is attended by a redistribution of heat; a combination of several gaseous molecules to form one fluid molecule is here said to occur. This hypothesis of change of molecular weight may be applied with equal correctness in explaining the phenomena attending fusion, and a distinction has ultimately to be drawn between gaseous, liquid, and crystalline molecules. To what extent such assumptions as these are of service in crystallography will be subsequently shown below.

¹ Groth, *Über die Molekularbeschaffenheit der Krystalle*, Munich, 1888.

CHAPTER VI.

SOLUTION AND SEPARATION.

WHILST the phenomena of melting and sublimation were long ago investigated and explained in all essential respects, the most contradictory hypotheses have always been entertained upon the subject of solution. Roughly speaking, two different views formerly prevailed amongst workers in this department of science; one party saw in solution a purely chemical process, whilst another considered it as a purely physical one. The principal adherents of the latter view were Graham, Brand, Daniel, Miller, Nicol, and Dossius, the former opinion being supported more especially by Berthelot, Cooke, and Henry; a sharp line of demarcation between the two parties was, however, never possible.

Recently, a considerable change in current views on this subject has resulted from the study of the so-called *osmotic pressure*, a factor which formerly received little attention, but which eventually proved of the utmost importance to the theory of solution. The osmotic pressure affords for all solutions characteristic constants which differ very widely for different solutions. The measurements require the employment of semipermeable media which will allow of the free passage of water—the solvent—whilst retaining the dissolved substance. Such a medium or vessel may be prepared by soaking unglazed earthenware cells, such as are used for fitting up galvanic batteries,

in a solution of copper sulphate and subsequently steeping them in potassium ferrocyanide solution. The pores of the earthenware thus become filled with insoluble copper ferrocyanide and a vessel is obtained which readily allows the passage of the water molecules but is impermeable to the dissolved substance.

If a cell prepared in this manner be filled with, say, a solution of sugar, securely closed and then placed in pure water, a remarkable phenomenon occurs; water passes through the cell walls and an increase in the internal pressure results. This pressure, which allows of easy measurement by means of a manometer, is termed the osmotic pressure; it is constant for the same solution, depends on the concentration, and increases until a maximum value is reached.

A very simple general law governs the osmotic pressure. *The osmotic pressure is directly proportional to the concentration of the solution*; so that, by doubling the concentration of the solution, the pressure itself is doubled. Considering a unit quantity of the substance dissolved in a varying quantity of solvent, the concentration of the solution is inversely proportional to its volume; consequently, the volume of the solution is also inversely proportional to the osmotic pressure. It is thus seen that the law stated above is identical in form with that which governs the relation between the volume and pressure of gases (Boyle's Law), and which states that the product of pressure and volume is a constant; the analogy between the gaseous and dissolved states may, however, be carried much further than this. As is well known, all gases, independently of their chemical composition, expand by $\frac{1}{273}$ rd of their volume at 0° for a rise of temperature of 1° ; and, if the volume be kept constant, the increment of pressure with change of temperature is also $\frac{1}{273}$ rd. The same is true of solutions.

The osmotic pressure increases as the temperature rises by $\frac{1}{273}$ rd of its value at 0° per 1° without reference to the chemical nature of the solution; the deviations from this simple law are scarcely greater than in the case of gases.

This close analogy existing between the gaseous and dissolved states is best expressed by the general law enunciated by van't Hoff in the following form. *The osmotic pressure of a solution has the same value as the pressure which the dissolved substance would exert if it were enclosed in the state of gas in the space occupied by the solution.* The molecules of gaseous substances, however different in chemical nature, occupy the same space; hence in a unit volume the pressure exerted by a gas is directly proportional to the number of molecules present. The same statement is also true for solutions: *The osmotic pressure is directly proportional to the number of molecules dissolved in unit volume of solution.* The numerous relations which in course of time have been established between vapour density and molecular weight can therefore be applied, collectively and without alteration, to the case of solutions.

Numerous exceptions to the general laws of gases were early discovered; it was observed, for instance, that the vapour density of ammonium salts is much smaller than is indicated by theory, or, what is the same thing, that the vapour tension is much greater than would be expected. All these anomalies, however, are only apparent, and were ultimately explained as resulting from a decomposition (dissociation) of the chemical molecules into two or more simpler ones on volatilization. A large number of soluble substances are known which deviate from van't Hoff's general law in an exactly similar manner; amongst these are acids, bases, and salts. Here, also, the theory which explains the gaseous phenomena, may be extended

to the case of solutions; in an aqueous solution of an acid, salt, or base, all or part of the dissolved molecules are dissociated into two or more lighter ones (ions). This hypothesis (dissociation hypothesis) is supported by a large number of facts, but more especially by the circumstance that all substances which undergo dissociation in aqueous solutions are electrolytes; the electrical conductivity of their aqueous solutions increases as the amount of dissociation becomes greater, or as the number of free ions present increases. Essential importance must be attributed to the fact that the dissociation hypothesis permits the application of very simple laws to the freezing points, as well as to the gaseous tensions, of solutions. The lowering of the freezing point by diminution of the vapour pressure in a solution is directly proportional to the number of dissolved molecules, independently of their chemical nature.

The process of solution may be conceived as completely parallel to that of evaporation simply by following up the above hypothesis. A liquid contained in a closed space evaporates until the space above the liquid is saturated with the vapour, or until the vapour tension has attained its maximum value and equilibrium is established between gas and liquid. This state of equilibrium or saturation is reached when the exchange of particles between the liquid and the superincumbent vapour proceeds at the same rate in each direction, i.e., when in unit time as many gaseous molecules return to the liquid as leave it and assume the gaseous state. Similarly, a solid in contact with a liquid, dissolves in it until the osmotic pressure of the solution reaches a maximum; and equilibrium or saturation is attained, when in unit time just as many molecules go into solution as return to the solid state. The point of saturation is hence determined by

the constant interchange between the solid substance and the solution, and a solution can only be described as saturated when it is in contact with the solid substance, just as a saturated vapour only exists in presence of the liquid. Many mistakes were formerly made by ignoring this condition.

The vapour tension of a liquid in all cases increases with a rise of temperature, and similarly, the solubility of a substance increases as the temperature rises. There are, however, a few exceptions to this rule; the solubility of some substances, such as calcium hydroxide and calcium isobutyrate, decreases as the temperature rises. These anomalous cases are yet further distinguished in that heat is not absorbed but liberated when the substance dissolves. Thus, the general relation always holds that the solubility of a substance is increased or decreased by a change of temperature as heat is absorbed or evolved respectively; the parallel between evaporation and solution is hence still complete, inasmuch as heat is always absorbed on evaporation.

CHAPTER VII.

WATER OF CRYSTALLIZATION.

CONSIDERABLE complexity is introduced into the phenomena of solution by the fact that many substances on separating in the crystalline form from their aqueous solutions, combine with so-called *water of crystallization*. That the appearance of this water in the solid state is due to some chemical cause, is apparent from its behaviour towards the substance with which it is combined. Some compounds lose their water of crystallization even at ordinary temperatures, and have to be prepared in freezing mixtures in order to avoid decomposition; such substances are termed *cryohydrates*. Other compounds containing water—the so-called *hygrohydrates*—are stable in moist air, but lose water on exposure to a dry atmosphere. Lastly, the amount of water of crystallization contained in a few substances is apparently dependent on the pressure of the surrounding atmosphere; these compounds may be termed *barohydrates*. Usually, a salt loses its water of crystallization, if not below 100° , at a little above that temperature. It is to be noted, however, that a substance containing several molecules of water of crystallization does not hold them all with the same degree of tenacity. The heat of hydration affords a measure of the attraction existing between the substance and the several molecules of water retained on crystal-

lization; for instance, strontium chloride and magnesium sulphate combine with successive molecules of water with the evolution of the quantities of heat indicated in the following table:—

SrCl_2 ; H_2O = + 5.62 cal.	MgSO_4 ; H_2O = + 6.98 cal.
SrCl_2 , H_2O ; H_2O = + 3.80 „	MgSO_4 , H_2O ; H_2O = + 2.30 „
SrCl_2 , $2\text{H}_2\text{O}$; H_2O = + 2.46 „	MgSO_4 , $2\text{H}_2\text{O}$; H_2O = + 3.40 „
SrCl_2 , $3\text{H}_2\text{O}$; H_2O = + 2.45 „	MgSO_4 , $3\text{H}_2\text{O}$; H_2O = + 3.40 „
SrCl_2 , $4\text{H}_2\text{O}$; H_2O = + 2.33 „	MgSO_4 , $4\text{H}_2\text{O}$; H_2O = + 2.17 „
SrCl_2 , $5\text{H}_2\text{O}$; H_2O = + 2.34 „	MgSO_4 , $5\text{H}_2\text{O}$; H_2O = + 2.17 „
	MgSO_4 , $6\text{H}_2\text{O}$; H_2O = + 3.66 „

An inspection of the table shows that the successive molecules of water are sometimes taken up with the evolution of a similar quantity of heat; this should be due to the identical relations of such water molecules to the compound. The first molecule of water is held with especial firmness in the two instances cited; as is borne out by the fact that a much higher temperature is required to expel this molecule. On heating crystalline magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), six molecules of water are lost at 132° , whilst the last is only completely eliminated at 210° .

The observation that some salts do not give off their water of crystallization all at once, but that a certain proportion is retained at a higher temperature than the rest, was made many years ago by Graham; he termed this firmly-held water, *water of halhydratation*, to distinguish it from true water of crystallization, which is more easily expelled. Erlenmeyer considered the water of halhydratation as water of constitution; the compound of one molecule of water with magnesium sulphate ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) being supposed to possess the constitution $\text{OH} \cdot \text{SO}_2 \cdot \text{O} \cdot \text{Mg} \cdot \text{OH}$. A similar assumption may be made for most substances containing one molecule of water of halhydratation, so that they may be represented as half basic, half acid salts.

That an essential difference exists between ordinary water of crystallization and water of constitution is plainly indicated by a number of facts. Thorpe and Watts observed that the water of constitution occupies a smaller volume when the compound is dissolved in water than the ordinary water of crystallization; the latter being in this respect indistinguishable from the water in which the substance is dissolved. A similar distinction is indicated by the experiments of E. Wiedemann, who found that salts containing water of crystallization possess a large coefficient of thermal expansion, and that the change of volume due to fusion alone is very small; substances containing only water of constitution, however, behave quite differently in this respect.

It has been long supposed that water of crystallization remains in the combined state in aqueous solutions of the substances; certain colour changes strongly favour this view. A solution of the monosymmetric cobalt chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, possesses a red colour, similar to that of the solid salt. On heating the solution to 120° , however, or on adding concentrated hydrochloric acid to it, the colour changes to blue, and from this blue solution a blue salt of the composition, $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, separates. Wiedemann's experiments show that the conversion of the red salt into the blue one in the solution is not instantaneous; the course of the change can be followed quantitatively by colorimetric measurements. According to recent investigations, the colour of a completely dissociated electrolyte is obtained by adding the colours of its two ions; consequently, since the Cl-ion is colourless, these colour changes are just as probably caused by a change in the Co-ion as by the existence of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, in the solution.

A saturated solution of a substance can only exist in

contact with the solid substance (see p. 28) ; if the latter be capable of taking up water of crystallization a rigid distinction must be made between the solubilities of the anhydrous and hydrated compounds. The solubility in water of hydrated sodium sulphate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, increases as the temperature rises until $+33^\circ$ is reached ; on further heating the mass of salt and water, less and less sodium sulphate is retained in solution, until at 100° the solubility is only about one half as great as at 33° . The old explanation of this phenomenon is that below 33° , hydrated salt is present as such in the solution, and above 33° , anhydrous salt ; this view is, however, erroneous, inasmuch as no indication of abnormal behaviour at 33° can be obtained from other properties of solutions of sodium sulphate.

A more probable explanation of these phenomena is that $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, only exists below 33° . On heating above this temperature, the crystals melt and anhydrous salt separates. The break in the solubility curve at 33° does not indicate that different salts exist in solution, but rather that different salts are *in contact* with the solution. The solubility between 0° and 33° is that of the hydrated salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and above 33° , that of the anhydrous salt, Na_2SO_4 ; the two curves cut each other at 33° . The solubility curve of the anhydrous salt may be traced below 33° by adding this salt to the solution ; far more of it dissolves than corresponds to the solubility of the decahydrated salt. Such a solution is hence *supersaturated* with respect to the latter salt, and if a crystal of it be dropped into the solution, immediate separation of this salt occurs, and the solution will dissolve no more anhydrous salt whilst still in contact with the hydrated one.

Another hydrated sodium sulphate, $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, is

also known; it is more soluble than the decahydrated compound, and a solution of it can hence be prepared which immediately crystallizes on contact with a crystal of $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$. By cooling such a solution it becomes also supersaturated towards $\text{Na}_2\text{SO}_4, 7\text{H}_2\text{O}$; on adding to the solution a crystal of either $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$, or $\text{Na}_2\text{SO}_4, 7\text{H}_2\text{O}$, the kind of salt added is at once deposited. Phenomena of this kind are incomprehensible if the water of crystallization exists already combined in the solution.

The behaviour of supersaturated solutions may be completely explained upon the lines indicated in the preceding pages. If a solution be cooled or allowed to evaporate, there is at first no cause for the separation of solid matter. At length, however, the osmotic pressure in the solution exceeds the solution pressure of one of the salts capable of separating, and on adding a solid fragment of the latter, rapid separation of the salt occurs and continues until equilibrium is established. Solutions which behave thus are termed supersaturated. Clearly, however, the idea of supersaturation, just as that of saturation, can only be used with reference to some definite substance; supersaturation otherwise becomes a meaningless term. The observations of Coppet on the freezing points of supersaturated solutions are quite in accordance with the views expressed above. The regularities observed differ in no way from those presented by ordinary solutions.

A correct appreciation of these relations is most easily arrived at by a consideration of the results obtained by Willard Gibbs. If n bodies in contact are present in $(n + 2)$ forms or '*phases*,' equilibrium between these phases will only occur at one fixed temperature and pressure; if only $(n + 1)$ phases occur together, equilibrium can be established throughout a certain range of temperature. Each temperature, however, corresponds to one and only one

pressure. If fewer than $(n+1)$ phases are concerned, equilibrium exists at any temperature. If two substances, such as a salt and water, be contained in a closed vessel, the three possible phases, i.e. salt, solution, and aqueous vapour, are in equilibrium through a wide range of temperature; each temperature, however, corresponds to one and only one vapour pressure, and conversely a given vapour pressure occurs only at one fixed temperature. Under ordinary circumstances solutions are operated with in open vessels; no independent vapour pressure can be set up in such cases, the solution remaining always under atmospheric pressure. This pressure (1 atmos.) may be taken as constant without appreciable error, and hence the vapour no longer operates as one of the three phases; the conditions of equilibrium are thus unchanged. In an open vessel equilibrium can be established at different temperatures between a salt and water. If the number of phases possible under these conditions is capable of increase, equilibrium should only exist at one definite temperature, the temperature corresponding to the fixed atmospheric pressure. Such a change in the number of phases comes into operation in the case of a salt which takes up water of crystallization, as, for example, sodium sulphate. Thus, solid anhydrous sodium sulphate, Na_2SO_4 , and solid hydrated sodium sulphate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, in contact with each other and with the solution, should be in equilibrium at one and only one temperature; this result is confirmed by experience, the temperature of equilibrium being $+33^\circ$, the melting point of the decahydrated salt. Above this temperature the salt dissociates into water and anhydrous sodium sulphate; below 33° the latter salt dissolves and subsequently separates as the hydrated salt.

The relations between the two hydrated salts $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ are obviously very similar to

the above ; these two substances plainly cannot separate together from the solution, and can only be in equilibrium with the solution at one fixed temperature. Directly the temperature becomes higher or lower than this, the one salt becomes converted into the other by addition or loss of water. Speaking generally, therefore, a salt cannot separate from one and the same solution in combination with two different proportions of water of crystallization. The existence of three salts containing different amounts of water of crystallization, such as Na_2SO_4 , $\text{Na}_2\text{SO}_4, 7 \text{H}_2\text{O}$, and $\text{Na}_2\text{SO}_4, 10 \text{H}_2\text{O}$, in equilibrium and in contact with the same solution is impossible under any conditions.

CHAPTER VIII.

DOUBLE SALTS.

THE formation of so-called double salts introduces a complication into the study of the nature of solution similar to that caused by the combination of a salt with water of crystallization. A double salt is a chemical compound of two salts, and is obtained when solutions of these components are mixed and allowed to crystallize. The chemical affinity of the constituent salts for each other is generally very slight, and comparable in degree with that by which water of crystallization is held. The question whether the constituent salts exist in the combined form in the solution of the double salt, or whether combination only occurs on crystallization, is of even greater interest in this case, than in that of water of crystallization. Up to the present, the matter has been investigated altogether by thermo-chemical methods, and by the study of diffusion. From a thermo-chemical point of view, the existence of a double salt in solution would be established only if on mixing solutions of the component salts, an absorption or evolution of heat, due to chemical action, were to occur. Such a change is observed in the case of but few double compounds, such as the double cyanides; the existence of double salts in solution must then in general be denied. This conclusion is opposed by certain experiments on diffusion. Rüdorff observed that on allowing a solution of

potassium copper sulphate, $K_2SO_4 \cdot CuSO_4 \cdot 6H_2O$, to diffuse, the liquid passing through the membrane contained the metals in the proportions in which they are present in the solid salt; this result is the more significant, inasmuch as potassium sulphate alone diffuses far more rapidly than copper sulphate. It would thus seem to follow that this double salt does exist in solution, although, on mixing solutions of the component salts, no evolution of heat occurs. The explanation of this apparent anomaly was given by Trevor¹; he repeated Rüdorff's experiments, examining the diffused solution, however, from time to time, not as the previous observer had done, merely analyzing the solution after the expiration of some long time. The composition of the solution diffusing at 16° was found to change as shown in the following table:—

Time in hours . .	1	1.5	3.5	5.5	7.5	9.5	10.5	30.5
Percentage of $CuSO_4$ } molecules in mixture of diffused salts }	20.7	22.1	23.2	25.6	26.2	32.9	47.0	50.1

The alteration in composition of the diffusate is explained by the fact that solid double salt was placed in the solution to ensure saturation during the process of diffusion. From an inspection of the figures representing the amount of copper sulphate present in the diffusate a short time after diffusion commenced, it is obvious that the potassium sulphate diffuses much more rapidly than the copper salt; as the solution thus becomes richer and richer in copper sulphate the number of molecules of the latter passing through becomes greater and greater, until at the end of thirty hours the constituent salts travel through at equimolecular

¹ *Zeitsch. f. physik. Chem.* vii. 468.

rates. At this period, however, the residual solution was found to contain 65.3 molecules of copper sulphate and 34.7 of potassium salt per 100 of the mixture. When the amount of copper sulphate in the solution subjected to diffusion was prevented from exceeding that indicated by the composition of the double salt, by passing a continuous stream of a saturated solution of the latter through the diffusion vessel, 85.2 molecules of potassium sulphate traversed the porous medium to every 14.8 of copper sulphate; the experiment was conducted at 14.7° . This velocity ratio of diffusion of the two salts is identical with the velocity ratio of the single salts; it must therefore be concluded that no combination between the component sulphates exists in the saturated solution of this double salt.

A similar behaviour is exhibited by most double salts; in a certain number, however, combination does take place in solution. Amongst these latter are found a number of double cyanides and double chlorides; on mixing aqueous solutions of their constituent salts a change of temperature occurs owing to absorption or liberation of heat. Such compounds as these are hence no longer classified with the true double salts which completely dissociate on solution. The best criterion as to the existence or non-existence of the double compound in the dissolved state, is found in the behaviour of the solution on electrolysis. When an aqueous solution of one of the double cyanides or double chlorides is electrolyzed, both metals do not separate at the cathode, but one of them appears at the anode with the acid radicle. A solution of sodium platinochloride, for instance, on decomposition by the electric current, yields sodium as the cation, whilst the heavy metal goes with the other anion to the positive electrode. On electrolysis of the double salts proper, as,

for example, the double sulphates, both metals appear at the cathode; in this case the constituent salts are not combined in solution, whilst in solutions of the double cyanides combination does exist.

No sharp line of distinction can, however, be drawn between the two classes of salts. Certain substances, of which potassium cadmium iodide is one, when electrolyzed in dilute solutions behave as a mixture of the constituent salts, and in concentrated solutions as a compound of those components.

A ready explanation of the phenomena attending the solution of double salts is found in Willard Gibbs' phase rules. In general, equilibrium can be established between two salts and their aqueous solution in an open vessel through a certain range of temperature, three phases existing. The pressure, however, being constant, the equilibrium is defined at each temperature; it would hence be expected that if two salts rest in contact with their solution, the latter should always possess the same composition at the same temperature. The composition of the solution should also be independent of the weight of the mixture of solid salts with which it is in contact. Most pairs of salts do behave thus; many salts, however, are anomalous in this respect, and allow of the preparation of several saturated solutions which at one and the same temperature contain the two salts in different proportions. Such pairs of salts are those which are capable of combining to yield double salts, and their peculiar behaviour is readily explicable. For, if the two salts A and B can combine to form a double salt, AB, a fourth phase is possible. Three substances (water and two salts), if present in four phases, can only be in equilibrium in an open vessel at one fixed temperature; if the three solid phases, A, B, and AB, are brought into the solution at any

temperature but this, readjustment will proceed until equilibrium is restored by the total conversion of one of the solid phases into either one of the other two. This readjustment may, however, take different directions. The double salt AB may separate, being formed by the solution of the simple salts A and B; equilibrium will then occur when one of the latter is wholly consumed and the solution is saturated with respect to the remaining simple salt and the double one. The final result, as regards the composition of the saturated solution, depends obviously upon the proportions in which the simple salts A and B were originally present. Another possible case is realized if the solution wholly consumes both simple salts and remains saturated with respect to the double salt AB alone. Under certain conditions the change may proceed in yet another direction, the double salt AB may dissolve whilst the simple salts A and B are thrown out of solution; equilibrium will then be established when the double salt has been completely consumed, and the solution remains saturated with respect to the two simple salts. Which kind of adjustment or equilibrium will occur in any special case naturally depends, first, on the solubility of the individual salts A, B, and AB, and secondly, on the proportions in which they are originally present in contact with the solution. In general, then, four distinct states of saturation-equilibrium are possible under atmospheric pressure for a pair of salts capable of forming a double salt; the solution may be saturated—

1. With respect to the double salt AB alone.
2. With respect to the double salt AB and the simple salt A.
3. With respect to the double salt AB and the simple salt B.
4. With respect to both the simple salts A and B.

On investigating the double sulphate of copper and potassium, $K_2SO_4 \cdot CuSO_4 \cdot 6H_2O$, Trevor found that the four possible cases of equilibrium enumerated above are realized under the following conditions:—

1. When the solution contains 11.14 per cent of the double salt.
2. When the solution contains 4.04 per cent of K_2SO_4 .
3. When the solution contains 1.44 per cent of $CuSO_4$.
4. When the solution contains 5.2 per cent of K_2SO_4 and 10.4 per cent of $CuSO_4$.

Saturated solutions possessing definite compositions¹ between the above limits cannot be prepared; readjustment always occurs, until one of the four kinds of equilibrium is established. All double salts behave similarly, so that the phenomena of replacement which have been observed for many years by Karsten, von Hauer and Rüdorff in connexion with such substances can be very simply explained.

¹ That is, saturated solutions at the temperature (25°) to which the numbers given above refer: the composition of the saturated solutions representing these four states of equilibrium would of course change with the temperature.

CHAPTER IX.

ORIGIN AND GROWTH OF CRYSTALS.

ONE of the most important problems of science relates to the origin and growth of crystals, and the empirical laws which govern crystallization. The importance of this question is only second in magnitude to that of the beginning and development of living organisms, and yet but little attention has hitherto been paid to it. The improvement of the microscope was accompanied by remarkable progress in the study of anatomy, physiology, and the life history of plants and animals; the value of this instrument in the investigation of the phenomena attending crystallization was, however, not recognized until the work of Sorby in 1858. Before that time numerous observations on the process of crystallization had been made, but the results were very unsatisfactory; and interest in the subject had suffered considerable diminution, owing to the recollection of the many futile investigations undertaken from rashly speculative premises in the hope of arriving at valuable theoretical results. On the whole, however, as the microscopic examination of rocks gained in importance from the work of Sorby, Vogelsang, Zirkel, and Rosenbusch, and the methods of recognizing and examining micro-crystals became more perfect, attention was more and more directed towards the question of the formation of crystals.

In the preceding chapter it is pointed out that crystals may be produced by three different methods, i. e., by separation of the solid substance from the gaseous, molten, or dissolved state. Whether chemical change occurs during the deposition is not of prime importance, since a chemical precipitate is only obtained in the crystalline condition when the solid substance is, to a certain extent, soluble in the solution from which it is thrown down.

The physical laws governing these three methods of formation of crystals have been fully discussed above, and show such complete accord in all essential respects, that what is true for the separation of crystals from a liquid solvent, may be at once applied to the two other methods by which crystals may be formed. Two cases of crystallization are, however, hardly embraced by either of the three general methods enumerated above; crystals may be formed by electrolysis of a metallic solution, or by the conversion of one solid physical isomeride of a substance into another. Leaving these two cases out of consideration, the empirical law governing crystallization may be stated in the following terms. *When a substance separates from a solution in the crystalline form, owing to withdrawal of the solvent, the crystals are the more irregular in shape, in proportion as the separation occurs with greater rapidity, in proportion as the solvent is more viscid, and in proportion as the substance is less soluble*¹. This statement applies more particularly to crystallization from a solvent, as the process of crystallization from the molten or gaseous state can only be followed with difficulty, when at all, by microscopic observation. Crystals bounded by plane faces, showing no re-entrant angles, are only obtained if the growth proceeds normally; by the action, however, of certain imperfectly understood disturbing influences, such re-entrant angles are formed,

¹ Lehmann, *Zeitsch. f. Kryst.* i. 453.

and very quickly develop themselves over the whole mass of the crystal, at a rapidly increasing rate. A secondary auxiliary growth is then deposited on this, then a tertiary one, and so on; the crystal thus ultimately becomes bounded by curved faces, or by plane surfaces showing re-entrant angles. During this action the structure remains quite regular, and, if the conditions of normal growth be re-established, the gaps quickly become filled up, and a perfectly regular crystal results from the crystalline skeleton; the latter is, however, readily distinguished from the normal growth by the presence of small cavities containing liquid. If the conditions are so altered that the habit of the crystal is changed, an alteration of the axes of maximum growth always results, and in such a manner, that the most acute parts of the crystal remain the parts of most rapid growth.

CHAPTER X.

FORMATION OF CRYSTALS. CRYSTALLITES.

ACCORDING to the most generally recognized theory, the formation of a crystal results from a regular deposition of its smallest particles. In the formation of a crystalline individual, therefore, the freely moving liquid molecules present in the solution must lose their independent motion and assume some definite position of equilibrium, by the operation of their internal forces. Many attempts have been made to follow this process by the aid of the microscope; these attempts have, however, resulted in failure, as will readily be understood when it is considered that, according to physical investigations, the molecules or their spheres of action would have to be some thousand times greater than they actually are, in order to be perceived with the aid of the most powerful instruments. There is, further, little hope of future success in this direction, for even with the instruments now in use, it can be seen that diffraction phenomena will soon limit the application of greater magnifying powers. If, however, we cannot hope to observe the first stages of crystalline development by means of the microscope, the work already done in this direction possesses the greatest interest.

The earliest investigation instituted with the view of founding a theory of the genesis of crystals upon micro-

scopic observations appears to be that of Link¹. He found, more particularly in the case of calcium carbonate, that the deposit or precipitate first appears in the form of tiny liquid globules, which subsequently pass from this intermediate stage into the solid crystalline condition. Schmidt² was led to a similar conclusion by an investigation of asarone, a substance extracted from the roots of *Asarum europæum*; the addition of water to an alcoholic solution of this compound causes a turbidity which on microscopic examination is found to consist of numbers of minute spheres suspended in the solution; after a short time, these easily movable minute drops unite in fours, and subsequently fall together building up a sharply-defined figure. The latter then continues growing by the addition of more tiny globules until a complete crystalline individual ultimately results. Frankenheim, from very comprehensive experiments on this subject, drew the conclusion that crystallization is primarily due to the formation of tiny supersaturated globules; these then become more and more free from solvent, and gradually solidify to small isotropic spheres. These particles received from Vogelsang³ the name of *globulites*; he observed their formation during the evaporation of a carbon bisulphide solution of sulphur thickened with canada balsam. Vogelsang recognized these globulites as an embryonic state of the true crystalline form; the time of duration of the globulitic state is mainly dependent on the viscosity of the solution. Vogelsang thus describes the further development of the globulites. 'The globulites are endowed with a certain regular molecular motion (force of crystallization) by virtue of which they are enabled to attract one another, to group themselves together, and to combine or arrange themselves in definite

¹ Pogg. Ann. 46, 258 (1839).

² Lieb. Ann. 53, 171 (1845).

³ Die Krystalliten, Bonn, 1875.

forms. The attractive forces causing this arrangement are not equal in all directions, but are in general symmetrically distributed, and are more or less influenced in their action by the resistance introduced by the physical conditions of the surrounding medium. If the direct, complete polyhedral grouping together of several globulites is prevented by external influences, transition forms—regular aggregates of globulites—known as *crystallites* are produced.’

If the resistance exerted by the solvent is considerable, the globulites at first arrange themselves in rows; these figures, resembling strings of beads, are known as *margarites*. Several of these margarites then amalgamate, giving acicular or acutely conical forms, termed *longulites*; the longulites are, however, frequently formed directly from the globulites.

The so-called *crystalloids* represent a still higher stage in the development of crystallites; they possess a simple characteristic form, and are frequently doubly refracting. The most perfectly developed form of the crystallite is the complete crystal; according to Vogelsang, however, this completion can only take place when the solvent opposes but a slight resistance to the operation of the molecular forces acting between the globulites, for without further aggregation of the globulites the finished crystal cannot be formed¹.

Such an explanation of the process of crystallization possesses many attractions. It affords a simple explanation of a fact well known to every analyst, i.e., that precipitates, such as ammonium magnesium phosphate, frequently do not completely separate from the solution immediately after deposition commences, but only after long standing. Addition of a trace of some solid substance, or vigorous agitation of the liquid, exerts a great influence on the separation. Further, it renders comprehensible the

¹ Vogelsang, *Die Krystalliten*.

fact that freshly deposited precipitates often pass readily through a filter paper, and only lose this property after long standing. Again, a most simple explanation is apparently afforded of numerous phenomena of supersaturation of solutions containing substances which do not crystallize with water.

The theory developed by Vogelsang has not been accepted altogether without opposition. Behrens¹ argues from many interesting experiments that a distinction must be drawn between continuously and discontinuously developed crystals; only the latter, he considers, owe their formation to globulites. Behrens agrees with Vogelsang in assigning the cause of these endeavours to separate in the crystalline form, to an orientated distribution of the attractive forces; he arrives at this belief principally on the ground of observations made on picric acid and its salts. Clearly such a supposition affords a ready explanation of the frequent occurrence of skeletal growths.

Knop², similarly, by the supposition of a non-uniform distribution of the forces of crystallization about axes of maximum attraction, has explained certain phenomena of growth observed by him amongst the chlorides of the alkali metals; Sadebeck³ subsequently employed the same line of argument in a similar manner. Such hypotheses as these must, however, be regarded as erroneous and superfluous; Lehmann has furnished⁴ an explanation of the simplest kind which holds with considerable consistency for most of the phenomena noticed in the course of crystalline development, and demands no such assumptions as had previously been made. The steps in the formation of crystallites and in the growth of crystals,

¹ *Die Krystalliten*, Kiel, 1874.

² *Molekularkonstitution und Wachsthum der Krystalle*, Leipzig, 1867.

³ *Angewandte Krystallographie*, 1876.

⁴ *Zeitsch. f. Kryst.* i. 453.

must, moreover, be regarded as of an entirely different character from those above described. According to Lehmann, it is absolutely unnecessary to make any assumption of the operation of polar attractive forces, even to explain the combination of the globulites; a satisfactory explanation of the facts is found in the molecular movements (Brownian or pedetic motion) peculiar to the globulites, and in the currents caused by capillary forces. It can thus be shown that no polarized or orientated forces are at work during the growth of crystals. Should the direction of most rapid crystalline growth be also that of maximum attraction, then during a reversal of the process of growth by re-solution of the crystal under the conditions existing whilst the rudimentary skeletal form was built up, this direction of greatest rapidity of growth should be the one most slowly attacked during re-solution. The opposite of this is, however, found to be true. If a skeletal form be dissolved under the conditions which held during its growth, the sharp edges disappear most rapidly, and shortly before complete solution occurs, the mass invariably becomes of a spherical or ellipsoidal shape.

CHAPTER XI.

THE PROCESS OF CRYSTALLINE GROWTH.

AN explanation of all the phenomena attending the growth of a crystal was sought for and found by Lehmann in the variations in the concentration of the solution immediately surrounding the growing crystal. He concluded, that if a crystal be placed in an exactly saturated solution of the substance, further growth is impossible, but can only occur when the solution increases in concentration. It is consequently necessary to crystalline growth that a certain *supersaturation*, however small, should be set up; on introducing a crystal at any point in such a supersaturated solution, the solution in the immediate neighbourhood of the crystal will become impoverished, and growth will therefore be arrested until the original state of supersaturation is restored by diffusion from the surrounding liquid. The concentration in the vicinity of the crystal is consequently dependent, firstly, on the rapidity of crystalline growth and, secondly, on the strength of the diffusion currents. The greater the first is in comparison with the second, the more considerable will the disturbances of the concentration become; of what kind these disturbances are, may be gathered from the following discussion. Suppose an ideal case, in which the crystal only withdraws matter from the solution, without itself at the same time increasing in size, and in which the

substance withdrawn from the solution is continually and regularly replaced by diffusion currents; the crystal surface will evidently be a 'surface of equal potential,' since the same degree of concentration—saturation—exists all over it. Similarly, a sphere described about the middle point of the crystal and sufficiently distant from it, is also a surface of equal potential, since the concentration prevailing all over it is appreciably the same as that of the liquid far from the crystal. The difference of concentration between these two surfaces is the same in all directions; the distance between them varies, however, in accordance with the shape of the crystal. Any intermediate surface of equal potential will be one intermediate in shape between the crystal and the sphere, and will project most where the edges and corners of the crystal stand out; these parts, then, are those at which the surfaces of equal concentration are nearest to each other, and consequently also the strongest diffusion currents occur.

A very good idea of the actual course followed during growth is obtained, by supposing the approximate conditions attending crystallization in the ideal case to be altered at very short intervals. Suppose the crystal to have grown under the ideal conditions mentioned above; its volume at the beginning of the second small interval of time is greater at every point than that during the first period of time, by a quantity proportional to the amount of substance deposited there. Further, the amount of dissolved matter in the immediate vicinity of the crystal is less by the amount which diffusion has failed to replace; the crystal is thus surrounded by a layer of dilute solution. Obviously, under such circumstances, further growth is for the moment impossible, and can only again proceed when a certain minimum supersaturation of the solution is once more established around the crystal; thus, the conditions

are once more the same as at the beginning of the first period of time. Now, this cycle of operations will not be of the same periodicity at all positions on the surface, but will be more quickly performed at those points against which the strongest diffusion currents play, and at which, consequently, growth recommences most rapidly. By adding together these small intervals of time and the small increments of the work of crystallization performed during them, it is easily seen that the crystal grows most rapidly at its corners and edges; in these directions indeed, growth proceeds with ever accelerated velocity since the amount of projection of the edges continually increases. The acceleration must be a decreasing one, inasmuch as a decrease in concentration causes a diminution in the speed of growth. Further, renewal of the supersaturation by cooling will cease so soon as the temperature of the solution attains that of surrounding bodies.

If the concentration of the solution decrease to such an extent that the crystal scarcely increases further in size, the growth will again become regular; the skeletal outline of the crystal will become filled in and the edges and corners of the crystal will appear very sharply and regularly defined. The crystal will now behave like an irregular crystalline fragment, irregularities in the surface being gradually filled up, until at length the complete form is attained. In general, therefore, a crystal growing with sufficient rapidity in a solution in which diffusion does not proceed satisfactorily, will grow most rapidly in the direction in which the crystal is most acute. Further, although the speed at which the substance separates may be increased by rapid evaporation or by cooling, the diffusion is, at the same time, hindered by increased viscosity of the solution or the decreased solubility of the substance. The general law of growth enunciated above,

or at least the principle underlying it, may thus be explained on theoretical grounds.

It is easily seen from the foregoing that the speed of growth should vary with the habit of the crystal; the formation of so-called secondary and tertiary branches can also be readily accounted for. The curved contour lines of the first single stem of growth endeavour, in accordance with a general property of crystals, to become true crystalline faces. In the first place then a secondary offshoot will form upon the side face of the parent stem and in the neighbourhood of the outgrowing point, but outside the special area which alone is sufficiently and continuously supplied with the materials for growth. The new offshoot will then be exposed to the full action of the diffusion current, which will thus adopt a new direction and therefore strike the offshoot with increasing velocity, forming a complete secondary branch. The primary stem will by this time have considerably increased in length, and a new secondary branch will spring from it at a point outside the range of influence of the first, later on a third will make its appearance, and so on. During the growth of the parent stem, therefore, its sides will become studded with secondary branches, which should naturally be parallel to each other. In an exactly similar manner, tertiary branches will spring from these secondary ones, and so on. This explanation of the secondary and tertiary growths which was given by Lehmann is in very satisfactory accordance with the observed phenomena, and is probably a true one. It may indeed be objected that the fundamental assumptions respecting the concentration of the solution round the crystal might not represent the truth; it might be supposed that the solution in the immediate vicinity of the crystal is more concentrated owing to some local surface action. Lehmann has, however, shown that the

area of relatively dilute solution round the crystal, which is essential to the theory, does in reality exist, and may be recognized by the following phenomena :—1. The difference of colour of the solution in the neighbourhood of the crystal. 2. The currents in the liquid caused by variations in the density of the latter. 3. The partial cessation of growth ensuing when two crystals are placed near each other in the solution. 4. The phenomena of dissociation observed in the vicinity of a growing crystal. 5. The dissolution of more easily soluble modifications of the substance in the neighbourhood of a growing crystal. 6. The solution of compounds containing water, or of physically isomeric modifications of a substance, near to a growing crystal of another compound or modification. 7. The solution and chemical changes of foreign bodies. 8. The variations in the refractive index of the solution near the growing crystal. 9. The currents induced in the solution by changes in the operative capillary forces. The two cases of formation of crystals additional to the foregoing, i. e., that depending on the changes of physically isomeric modifications, and that attending electrolytic separation, are also readily dealt with by the above method of explanation. If the formation of the crystalline skeleton is not the result of maximum attraction in one special direction, but originates in powerful diffusion currents, such skeletal structures cannot be formed during change of one crystalline form into another in the solid state, since diffusion currents then naturally become impossible. This, however, certainly takes place, and has been shown to hold without exception in all the observed cases of this nature¹. Crystals of a stable modification, as a rule, develop in the mass of a more unstable modification with beautiful plane faces; in other cases, however, the new form grows

¹ Lehmann, *Zeitsch. f. Kryst.* i. 627.

irregularly. This latter phenomenon is, in all probability, conditioned by incomplete homogeneity of structure, internal tension, &c.

The electrolytic deposition of metals should naturally give rise to rudimentary forms of growth, such as occur in the crystallization of supersaturated solutions; the same considerations respecting the concentration of the solution in the vicinity of the growing crystals are evidently applicable to both cases, in so far as the quantity of undecomposed or undeposited substance is concerned. Besides this, however, a new factor comes into play, inasmuch as the first separation of substance or the most rapid deposition of crystal occurs at the point at which the difference of potential is the greatest. Since the maximum potential difference exists at the projecting points, no further discussion is necessary, inasmuch as what has been said respecting the surface of equal concentration round the growing crystal is equally valid for the surface of equal electrical potential.

This question has been specially examined experimentally by Lehmann; in his investigations a four-sided metal leaflet, resembling a crystal of metallic tin, was used as one electrode in a very dilute solution of boiled milk. The fatty globules served as non-conducting spheres, which on passage of an induction current acquired electrical polarity, and by aid of the microscope were seen to arrange themselves in clusters resembling strings of beads, in such a manner that the surface of equal potential projected furthest at the extreme corners of the metallic leaflet. Hence, using an actual crystal of tin and a solution of stannic chloride in place of a model and a solution of milk, the growth should be most rapid at the corners of the crystal; this was found by experiment to occur, although the observations could not be made with ease owing to

the fact that several crystalline individuals usually spring from the one electrode and thus break up the equipotential surface. Consequently, during the galvanic deposition of crystals, this distortion of the equipotential surface comes into play, in addition to the differences of the concentration of the solution. Since both influences act in the same direction, skeletal growths are very readily obtained in such cases; hence, in order to obtain well-developed crystals by electrolysis, it is necessary to employ very weak currents, so as to reduce the speed of growth to a minimum.

The value of Lehmann's theory of the growth of crystals rests not merely on its experimental basis, but is also enhanced by the ease with which it fully explains most phenomena of irregular development of crystals, more especially the following:—1. The increasingly accelerated growth of crystals at the corners, and the formation of secondary and tertiary branches. 2. The alterations in the directions of growth with the crystal habit. 3. The favourable influence on the formation of skeletal growths exerted by rapid deposition and sparing solubility of the substance, and by great viscosity of the solutions. 4. The tendency towards the assumption of a spherical form exhibited by dissolving crystals. 5. The non-occurrence of skeletal growths during molecular changes of physically isomeric substances. 6. The readiness with which skeletal forms are obtained during electrolytic separation.

It should be remarked that this theory of the growth of crystals, though so complete in itself, disregards altogether the fact that heat is liberated during the process of crystallization. This, as Wulff has remarked¹, must tend towards considerable complication of the process, although the final result might not be essentially changed. It should be remarked, that the formation of a layer of dilute

¹ *Zeitsch. f. Kryst.* ii. 120; compare Lehmann, *ibid.* x. 1, and xii. 391.

solution immediately round the crystal by separation of solid matter, acts in the same direction as the heat evolution attending that separation. Further, the influence of the heat evolution tends to increase the action exerted by the deposition of solid on the shape of the equipotential surface. The diffusion currents would thus be still more strongly directed against the edges and corners of the growing crystal. If the liberated heat itself cause diffusion currents, these would be of such a kind that on their increasing in strength owing to separation of substance, warm and light layers of liquid would be conducted away from the corners and edges of the crystal; for not only would heat be given up more readily from the crystal angles, but at those parts also the most rapid growth already occurs. Consequently, fresh supersaturated solution would be brought most rapidly to the sharp edges; the growth at these parts would thus not be hindered by the liberation of latent heat, but even promoted, and the convection currents would coincide in direction with the diffusion currents.

CHAPTER XII.

STRUCTURAL ANOMALIES.

A CONSIDERATION of the so-called *anomalies of crystalline structure* is of the same prime importance to a correct appreciation of the nature of the crystallizing process as a knowledge of the rudimentary forms of growth ; these anomalies have also been fully investigated by Lehmann. On the ground of his own observations and those of others, as well as on that of the microscopic investigation of rocks, the different cases of anomalous crystalline structure may be classified in two groups. During the formation of a crystal the arrangement of the crystalline elements may change in a perfectly continuous manner and thus cause the crystal to assume a curved form ; such an alteration may, however, also occur abruptly, giving rise to dendritic growths. Both cases almost invariably arise together.

The empirical law governing the occurrence of such anomalies may be stated as follows :—The free operation of the forces of crystallization is checked by either an increased viscosity of the solution or a decreased solubility of the substance, to an extent which more or less hinders the parallel deposition of the molecules. The force of crystallization does indeed resist these influences, for crystals which have become curved in consequence of these causes, seem, whilst they are still very thin, to strive against

the curving, and tend to become straighter on further growth; they exhibit signs of internal tension but are still distorted to a greater or less extent according to the prevailing conditions.

So-called dendritic growths frequently occur, especially when a crystal, during the process of growth, happens to meet some other solid body. The branching usually occurs in such a manner that the acutely developed parts of the crystal are split up into a brush-like form. The symmetry of growth is then still further destroyed in a somewhat similar manner by an apparent bending of the individual twigs, thus giving rise to curvature of the crystal as a whole.

All these phenomena can be completely explained by a consideration of the nature of solution. It will be at once apparent that if the solution attains so high a degree of viscosity as to approximate to the solid state, a point must at length be attained when the molecules are no longer capable of uniting to form a crystal. Just before reaching this state, however, the molecules will still be deposited, but with much greater difficulty than from more mobile solutions; the degree of supersaturation will hence have to increase considerably before separation can occur. This is, as a matter of fact, found to be true. A similar state of affairs occurs in the case of sparingly soluble substances, since the distribution of the dissolved matter through a relatively large quantity of liquid must be eminently unfavourable to the combination of the molecules. Now an increase in the degree of supersaturation carries with it a widening of the sphere of action of the crystal, that region in which the force of crystallization still exerts an appreciable opposition to the solvent action of the liquid; it is also to be observed that the force of crystallization, being a molecular force, rapidly decreases as the distance

increases. The greater, however, the distance from which the molecules are drawn for direct insertion in their positions in the crystalline edifice, and the more viscid the surrounding solution, so much the less is it possible that the molecules shall be properly orientated before deposition. It is hence readily seen that in such cases, irregular structures of the same kind as those actually observed should result; the accordance between theory and experiment is thus complete. If the molecules really possess a tendency to deposit themselves in parallel positions, they will strive to exercise this power, even if complete attainment of the end is impossible. Under such conditions a gradual deflexion of the direction of crystallization results; this is observed occurring in the most perfect manner in the growth of the brush-shaped forms spoken of above. If this ramification can proceed with equal ease in all directions, spherical forms consisting of numerous radially disposed individuals are produced; these are the so-called *sphærocrystals*. Sometimes the curvature is determined towards one or the other side; this is found to be more particularly the case, when the growing crystal possesses one oblique terminal face. One direction is then more subject to deflexion than another; further, it is seen that the curvature of the crystal changes with the development of one or another terminal face.

On bringing a curved crystal into more favourable conditions for growth, the new molecules which are deposited would naturally tend to arrange themselves regularly. A pressure would thus be exerted on the concave side and a pull on the convex one, so that the crystal should strive to straighten itself; experiment shows that this does actually occur.

A consideration of the extreme case, in which the solubility has decreased to insolubility, and the viscosity

has increased to solidity, shows that the substance must separate in an amorphous (or better, structureless) state, in which the molecules are deposited with an entire absence of regularity. In practice there are two, and only two, methods of obtaining a substance in the amorphous condition:—(1) By chemical precipitation of the substance from reagents in which it is absolutely insoluble, in which case the precipitate takes the form of a pellicle separating the two reacting liquids, as in the precipitation of metallic sulphides by ammonium sulphide; and (2) by rapid concentration or cooling of the viscous solution or molten magma to the solid state, as in the formation of amorphous sulphur or sulphur globulites.

Since, in the end, hindrances to crystallization consist principally in the immobility of the molecules, it might be expected that crystallization would attend artificial disturbances of the solid mass. This is, in fact, the case, for, on scratching or subjecting to pressure substances which do not possess extreme solidity or lack of viscosity, crystals invariably make their appearance and slowly grow, generally giving rise to sphærocrystals. This kind of 'devitrification' seems to proceed gradually and spontaneously during a long period of time, chance bringing several molecules together in such a manner that they can combine to form a crystalline nucleus. Several examples at least which illustrate this are known, such as the crystallization of amorphous sulphur and of certain slags. As to the extent to which the formation of a crystal is affected by the viscosity of the substance, it may be *a priori* assumed to be very different in different cases, according to the intensity of the force of crystallization. It may thus well occur, and is indeed frequently observed, that one constituent of a solution may separate only in sphærocrystals, whilst another component assumes almost its normal form.

So long as no means exist of accurately defining the 'force of crystallization' in its attractive and its directive capacities, so long will it be impossible to predict what particular degree of viscosity is necessary to the formation of spherulites of one or another substance.

The formation of twin-crystals, that is, the deposition of the molecules in regular, but not parallel, positions, must also be attributed to this inhibitive action of the solvent. This is demonstrated by the following experiment with barium chloride, a substance which under ordinary conditions possesses only a slight tendency to form twin-crystals. If a solution of barium chloride thickened with gum be concentrated or cooled, a deposit of beautiful tree-like crystals is obtained; the branches of these are the more numerous and delicate, as the solution is the more viscid and crystallization is the more rapid. Careful examination shows that the primary and secondary twigs are always in the position required by twinning. The frequent twinning observed on naturally occurring crystals is possibly due to this same cause, more especially as the substances concerned, are, for the most part, sparingly soluble, and are often deposited from viscous solutions. When easily soluble substances are dealt with, as is usual in the artificial preparation of crystals, twins are of comparatively rare occurrence. Although the factor essentially responsible for the structural anomalies of crystals deposited from dilute or viscous solutions, is the influence of the solvent on the forces of crystallization treated of above, other disturbing causes are frequently operative; these are partly connected with capillary forces, and partly with the force of crystallization of foreign substances. To the former category of disturbing influences must be relegated those forces which induce the continual renewal of a thin layer of liquid between a growing crystal and the solid wall of the

containing vessel; this influence is seen at work in the phenomenon of efflorescence.

Many phenomena which are as yet but incompletely understood belong to the second category; of which a very beautiful illustration is furnished by cupric chloride. This substance separates from its hot ammonium chloride solution in cruciform twin-crystals, but is deposited from its pure aqueous solution in beautiful lustrous needles. In general, this change in habit is more often shown if the mixed substances are chemically related or have some tendency to form double salts.

The influence of a foreign crystalline substance upon the crystallization of another compound is frequently shown in the regular growing together of two crystals of quite different kinds, as, for example, rutile and specular iron, copper pyrites and fahlore, soda and potash felspars, and also in the case of calcite and sodium nitrate where the one substance ultimately envelopes the other.

A complete explanation of all these phenomena will only be possible when the crystalline structure of each substance concerned is completely determined; the observation of such anomalies should, however, furnish many stepping stones towards the future attainment of such a knowledge.

CHAPTER XIII.

THE OCCURRENCE OF DIFFERENT SIMPLE CRYSTALLINE FORMS.

It is a generally known fact that the simple forms assumed by a substance may be quite different according as the conditions of crystallization vary. Certainly, many individual cases are known, in which a substance invariably takes up the same form during crystallization, but, as every chemist is aware, most substances show great variations in this respect. Thus, the form and habit of the individual crystals of a great number of minerals furnish a fairly trustworthy criterion of the locality from which they were originally obtained. Naturally, this dependence of crystalline form on the conditions of growth can only be conveniently traced with readily soluble substances. No satisfactory results have, however, been deduced from a very large number of experiments made by Frankenheim and others with the object of determining this relationship. Numerous facts have been collected, as, for example, that sodium chloride, which ordinarily crystallizes in cubes, separates in octahedra from a solution containing urea, caustic soda, potassium oxalate, &c., and that ammonium tartrate cannot be obtained in hemihedral forms from its pure aqueous solution, but only from one rendered impure by decomposition products, &c. The alums also crystallize from alkaline solutions in cubes instead of in the usual octahedral

form. Practically no explanation of these facts has yet been given, and no help is afforded by our present knowledge of the process of crystalline growth.

Recently, however, some slight grasp of these phenomena has been derived from purely theoretical considerations¹. The total energy of a solid or liquid body may be considered as made up of two parts; firstly, the energy possessed by the molecules in the interior of the mass, and secondly, the energy of the particles on the surface². A molecule upon the surface, or upon the boundary, between two media, possesses much less mobility than one situate in the interior of the mass; consequently, in increasing the surface area, work has to be done against the molecular forces. Since, now, whatever form a body assumes, its volume remains the same, the collective internal energy is independent of the form of the mass; the energy resident in the surface or boundary, however, increases as the surface increases. If the shape of a body changes, its total energy alters by an amount corresponding to the change in shape. But, as the energy possessed by a body always tends towards a minimum, the mass, unless prevented by some cause or other, will assume the shape which exposes the least possible surface. Thus, liquids, when free to alter their shape, take up a spherical or drop-like form. The unit of superficial or surface energy is represented by the capillary constant, A ; if all the faces of a crystal had the same capillary constant, the form ultimately obtained would necessarily be that of a sphere. If, however, several bounding faces be developed, having the areas $S, S_1, S_2, \dots S_n$ and the capillary constants $A, A_1, A_2, \dots A_n$ respectively, the most stable form will evidently be that for which the sum

¹ Curie, *Bull. Soc. Min.*, viii. 145. Liveing, *Camb. Phil. Soc.*, xiv, xv.

² Maxwell, *Theory of Heat*, 1885 Ed., p. 280.

$AS + A_1S_1 + A_2S_2 \dots + A_nS_n$ is the minimum. Since now all the physical characters of a crystal, and therefore also the cohesive forces, vary with the direction, it may reasonably be assumed that the capillary constants of the different crystal faces differ amongst themselves. It is of interest to note that only crystallographically different faces should differ in respect to superficial energy, whilst crystallographically identical faces would have the same surface energy.

It may be assumed *a priori* that the capillary constants of crystalline faces vary with the temperature, in addition to being influenced by the surrounding medium. The faces which should be developed and the relative speeds at which they should grow could now be determined, if the necessary numerical data were given, and no disturbance were introduced by structural anomalies. A complete experimental investigation of this explanation would present very great difficulty and has not yet been carried out; many observations, however, strongly support the theory, whilst none oppose it. If a crystal is placed in a saturated solution, it has the power of altering its shape, without, on the whole, either giving matter to, or absorbing it from, the mother liquor. Leaving the action of gravity out of account, such a change can only be caused under ordinary conditions and at constant temperature by some change in the energy of the surface of separation, and even if the temperature oscillate, no definite direction should be given to the deformation of the crystal. Such phenomena of deformation of crystals in definite directions may be pretty frequently observed in actual practice; as an example may be taken the well-known fact, that the larger crystals in a solution often tend to increase in size by absorbing the smaller ones. The theory described above is hence worthy of all attention.

Special interest attaches to this subject from the fact that Sohncke¹ has endeavoured to establish a relation between the surface energy of a crystal face and its so-called *face-density*; the latter represents the number of mass-points, which must be supposed to exist in unit area of such a face. From a consideration of the structure of particular crystals, Sohncke concludes that that crystalline plane which is the most thickly studded with mass-points occurs the most frequently as a crystalline face, being the most readily built up. It is hence clear that in a face of maximum face-density, no work remains for the molecular forces to perform, since the particles can come no nearer together; the surface energy of such a face is hence a minimum. These considerations thus lead to a kind of connexion between the internal structure of a crystal and its external form.

Sohncke has also attempted to demonstrate a relation between the principal cleavage form and the crystalline structure by somewhat similar means. His hypothesis, however, is not yet placed on a satisfactory basis, and its further description would necessitate a full account of the properties of space lattices and point systems.

¹ *Zeitsch. f. Kryst.* xiii. 221.

CHAPTER XIV.

GENERAL RULES FOR THE ARTIFICIAL PREPARATION OF CRYSTALS.

FROM the considerations brought forward in the foregoing chapter, it is evident that all endeavours to prepare crystals of the greatest possible perfection must be based on the following three principles. 1. The crystallization must proceed as slowly and uniformly as possible. 2. The solution or magma from which the crystals separate must possess the least possible viscosity. 3. The crystallizing substance must be present in the solution in the greatest possible quantity or must be readily soluble.

The length of time necessary for the formation of a homogeneous crystal is greater in proportion as conditions (2) and (3) are less completely fulfilled. The cultivation of good crystals should present little difficulty in the case of substances readily soluble in water, alcohol and similar liquids; this is generally found to hold good. In considering the few exceptional cases, it must not be forgotten that the power of crystallization of a substance is, in the end, a function of its chemical nature; hence, independently of the mere external conditions attending the crystallization, other influences may be at work.

The principle has been often enunciated that complete

immobility is necessary to the formation of good crystals, so that all shaking should be avoided as much as possible. This rule is, however, of only limited application ; Wulff¹ showed that it is not the motion of the solution *per se* which acts injuriously during the process of crystallization, but only a subsidiary action which accompanies the shaking. It has been shown above, that during evaporation and cooling, layers of different temperatures and different concentrations are formed in a crystallizing solution ; the heat liberated by the separation of solid also contributes towards this result. Under these conditions any agitation will cause the various liquid strata to mix directly, instead of becoming mixed by the slower process of diffusion ; further, a supersaturation will set in, in all those cases in which a rise of temperature of the solution is accompanied by a more than proportionate increase in the solubility of the dissolved substance. This latter is indeed usually the case, and agitation consequently occasions a sudden separation of the substance, which prevents the formation of good crystals. If, however, these layers of different temperatures and concentrations are never allowed to form in the solution, movement has no injurious effect. In the process of 'sugar boiling,' the solution is undoubtedly in a state of violent agitation, yet the most beautiful crystals frequently separate ; and Wulff moreover states that better and more regularly developed crystals are deposited from agitated solutions than from those kept at rest. In order that shaking should be without injurious effect, the following conditions must therefore be fulfilled. 1. The motion must be continuous, because during pauses layers of different temperatures and different concentrations would begin to form, and on recommencing the agitation partial supersaturation would set in and rapid crystallization would become possible.

¹ *Zeitsch. f. Kryst.* ii. 120.

2. The motion must be of such a kind that the growing crystals are continually washed into different positions, otherwise structural anomalies might easily make their appearance.

In this method of preparing crystals it is further necessary to bear in mind that a separation immediately attends the establishment of any considerable supersaturation in the solution, even during the continuance of the motion. If, therefore, the formation of a crystalline meal, which exercises so injurious an effect on the formation of well-developed individual crystals, is to be prevented, the decrease in the amount of substance held in solution, caused by cooling or by evaporation, must be brought about slowly; all the separating material will thus be taken up regularly and normally by the crystals already present. A regular distribution of the growing crystals throughout the whole mass of solution is also advantageous. Although some skill is necessary in order to obtain good crystals from shaken solutions, yet the method possesses many advantages. Evidently, the individual crystals thus obtained should be equally developed on all sides, and should realize to a greater or less extent the ideal crystalline form. This latter condition is ever of the greatest importance whenever a hemihedral or hemimorphic substance is being handled as well as in many other cases. The process is therefore well worthy of trial.

A general rule, which should also be observed during the artificial preparation of crystals, consists in the avoidance, as far as possible, of changes of temperature. A partial supersaturation of the solution always succeeds a fall in temperature, and thus a sudden separation can be readily caused; the small crystals so formed, however, are partially redissolved on warming. If the solution cannot be maintained at a constant temperature, it is at least well to take

the precaution of removing the crystals from the solution at a time when the temperature has reached a minimum. If this be not done, the crystals are often corroded or covered with etched-faces, and their measurement is consequently attended with unnecessary difficulty.

CHAPTER XV.

SPECIAL METHODS OF PREPARING CRYSTALS.

THE most important methods¹ which up to the present have been employed for the preparation of crystals may be divided into five groups, according as the substance separates from the gaseous, molten or dissolved state, or crystallization occurs through molecular change in the solid state, or by electrolytic deposition.

I. SUBLIMATION. As is well known, the process of depositing a substance in the crystalline form from the gaseous state is described as sublimation (p. 22). Two cases can, however, be distinguished, according as chemical change is or is not concerned.

1. *No chemical reaction occurs during the sublimation.* Certain substances, such as naphthalene and ammonium chloride, may be readily obtained in the crystalline state by heating them and subsequently cooling the vapour. In a similar manner, crystals of galena, blende, calomel, arsenic, &c., are frequently obtained during metallurgical operations when the air supply is cut off. The method of preparing artificial wurtzite (ZnS) must also be placed in this category. Deville and Troost heated amorphous, precipitated zinc sulphide, in a porcelain tube, in a current of hydrogen; the volatilized zinc sulphide was thus protected from the action

¹ Fuchs, *Die künstlich dargestellten Mineralien*, Harlem, 1872. Daubrée, *Études synthétiques de géologie expérimentale*, Paris, 1879.

of atmospheric oxygen and was deposited in crystals on the cooler parts of the tube.

2. *The process of sublimation is accompanied by chemical change.* Many non-volatile compounds can be obtained in a crystalline condition by chemical action between a volatile substance and a gas; the process of formation is thus combined with one of sublimation, and the crystallization occurs with corresponding slowness. Most of the metallic sulphides found in nature may be artificially obtained in crystals by such a method; stibnite, bismuthite, blende, greenockite, and copper and iron pyrites may be prepared in the crystalline state by strongly heating the corresponding metallic chlorides in a stream of hydrogen sulphide. Even minerals of such complex composition as red silver ore and fahlore can be synthesized in this way. If the metallic chlorides be heated in a current of steam, instead of in hydrogen sulphide, the crystalline oxides are obtained in place of the sulphides. Daubrée by this method prepared cassiterite, specular iron, and even quartz, whilst Hautefeuille synthesized rutile, and Senarmont obtained corundum. This kind of process is applicable in many cases and the products of the reaction are usually obtained in a crystalline state. Deville prepared magnetite by the action of ferric fluoride vapour on boric anhydride, and Daubrée prepared quartz and various crystalline silicates by the action of gaseous silicon tetrachloride on the alkaline earths heated to redness. Spinel, gahnite, willemite, and staurolite have also been synthesized by similar methods.

II. FUSION. The deposition of crystals from a molten magma fall in general under one of the following three heads:—1. When the solidifying substance is chemically homogeneous. 2. When the separation consists of only one constituent of the magma. 3. When the fusion is accompanied by chemical change.

1. *Crystallization from a homogeneous magma.* A series of elements, such as sulphur, copper, lead, silver, and bismuth, as well as many compounds, such as bismuthite, stibnite, olivine, augite, feldspar, and the easily fusible salts of the alkali metals, separate in crystals when melted and slowly cooled. The best individual crystals are usually obtained by breaking a hole in the solid crust formed on the surface of the cooling mass and pouring off the still liquid portion. It is, in many cases, unnecessary to melt the substance itself, as a mixture of the constituents in the proper proportions when heated gives the same result. Thus, Mitscherlich in 1823 obtained the cubic copper sulphide by melting two parts of copper with one part of sulphur; he also prepared augite in a similar manner from calcium silicate and magnesia. About the same time Berthier prepared various silicates artificially, and more recently Michel Lévy and Fouqué have been enabled to prepare all the more important silicates in the same way; amongst others feldspar, nepheline, and garnet.

2. *Crystallization of a dissolved substance from a molten magma.* Molten substances like water or alcohol can serve as solvents for other substances; on cooling or even before solidification of the magma the dissolved substance separates in the crystalline form. Thus, carbon dissolves in molten iron and partly separates in the form of graphite on solidification; Moissan has recently synthesized the diamond by a process similar to this. As early as 1845, Ebelmen employed boric anhydride as a solvent for the metallic oxides, obtaining them in crystals by evaporating off the boric oxide; corundum and spinel were obtained in crystals of 4 mm. length by this method. Olivine may be prepared by melting together a mixture of silica, magnesia, and boric anhydride; a solvent alkali, such as crude potash, may often be employed instead of boric anhydride, as in the preparation

of olivine. Crystals of perovskite are obtained on heating a mixture of titanite oxide, lime and an alkaline carbonate to fusion. Gustav Rose in many cases used sodium carbonate, borax and microcosmic salt as solvents, and by their aid prepared specular iron, anatase, and tridymite. Sodium chloride was also employed by Forchhammer in the synthesis of apatite ¹.

3. *Crystallization caused by chemical change in the molten condition.* The separation of a dissolved substance from a molten magma is frequently accompanied by chemical change, and it is then not always easy to determine whether the reaction was at an end before crystallization began, or whether the two processes proceeded more or less simultaneously and were thus mutually dependent. A typical case of this kind of crystallization is found in the preparation of barytes by Manross, by fusing a mixture of potassium sulphate and barium chloride. On lixiviating the cooled mass, potassium chloride dissolved, whilst the heavy spar remained in distinct crystals. By similar treatment, celestine is obtained from strontium chloride and potassium sulphate; anglesite, scheelite, and wulfenite can also be formed from the corresponding constituents. The chemical change is, however, not always of so simple a nature as in the above-mentioned cases, decomposition being sometimes caused by the heat. Thus, for example, Debray prepared crystalline magnetite by heating a mixture of iron sulphate and phosphate, whilst Kuhlmann synthesized the same mineral by fusing calcium chloride and ferrous sulphate. Further, Heintz obtained boracite crystals by fusing the constituents of the mineral with an excess of magnesium and sodium chlorides.

The separation of many silicates from artificial slags belongs properly to this division, since the body of the

¹ O. Schott. *Anorganische Schmelzverbindungen*, Brunswick, 1880.

slag has not quite the same composition as the crystals which are deposited, and the formation of the silicates composing the latter takes place during the cooling. A sharp distinction between cases (2) and (3) is, however, not always practicable.

III. SOLUTION. The preparation of crystals by separation of a substance from its solution in a liquid solvent surpasses all other methods in convenience and certainty; this process is therefore usually employed when the properties of the substance concerned allow of it. The principal solvent used is water, but organic liquids, such as alcohol, ether, petroleum, benzene, acetic acid, &c., find constant application, more especially in the crystallization of organic substances. The separation of a substance may result either from simple decrease in the quantity of substance capable of remaining in solution, or from a chemical reaction.

1. *Crystallization by evaporating or cooling the solution.* Since the solubility of a substance is generally less at low than at high temperatures, crystallization occurs on cooling a concentrated hot solution. The processes of crystallization by cooling the solution and by evaporating off the solvent, usually proceed side by side, the solution being cooled by spontaneous evaporation and again warmed by the latent heat of separation of the crystalline solid matter.

The more soluble substances, such as the chlorides, sulphates, nitrates, &c., are best obtained in good crystals by spontaneous evaporation of their solutions at as constant a temperature as possible. If the substance concerned is highly hygroscopic, the solution may be evaporated by heat, or an aqueous solution by standing in a closed vacuum space over sulphuric acid. Sparingly soluble substances may be often crystallized by carrying out both solution and separation at a high temperature

and under great pressure. Thus, Senarmont obtained crystalline barium sulphate by heating the freshly precipitated salt in a hermetically sealed glass tube with hydrochloric acid or sodium bicarbonate solution at about 250° for 60 hours. Similarly, bismuth sulphide was converted into bismuthite by heating with potassium sulphide, whilst arsenic trisulphide when heated with sodium bicarbonate solution yielded realgar. Wöhler converted apophyllite into well-defined crystals by heating it with water in closed tubes at 190° . It is a fact of the greatest importance to geology that quartz may be obtained by this wet method. A solution of silicic acid in dilute hydrochloric acid, best prepared by decomposing silicon tetrachloride with water, when heated in closed tubes at 200° – 300° , yields distinct crystals which may be identified with quartz in various ways.

A decrease in the amount of solid capable of remaining in solution may be brought about as follows. A layer of the pure solvent is first placed above a saturated solution of the substance, then a layer of another liquid miscible with the first, but in which the dissolved substance is more sparingly soluble; on allowing the whole to stand diffusion proceeds slowly and the sparingly soluble product of reaction separates in the crystalline form. If any difficulty be found in arranging the layers, they may be separated by a porous diaphragm, or a slow and regular mixture may be ensured by any other convenient method. By such a process as this, sulphur may be obtained in good crystals; its saturated solution in carbon bisulphide being first covered with a layer of the latter and then with a layer of alcohol, ether, oil, acetic acid or petroleum. Similarly, lead chloride may be obtained in crystals by placing layers of hydrochloric acid and water on its solution in hydrochloric acid.

Lastly, the separation of a dissolved solid substance may be brought about by putting into the saturated solution some other soluble substance; partial replacement of the one by the other substance then, as a rule, occurs, and the dissolved substance separates in crystals. Thus, on placing paraffin wax in a saturated solution of sulphur in carbon bisulphide, beautiful pyramids of sulphur are formed, and conversely by putting powdered sulphur into a solution of paraffin in carbon bisulphide, long lustrous needles of paraffin separate.

2. *Crystallization caused by chemical change.* In order to obtain difficultly soluble substances in a crystalline form, without the application of great pressure, it is sometimes convenient to prepare them by the interaction of soluble compounds. Naturally, such a separation should proceed comparatively slowly, so that sufficient time may be allowed for considerable quantities of the sparingly soluble substance to assume a regular structure or to crystallize. Macé obtained lead sulphate crystals at ordinary temperatures by this means; ferrous sulphate solution was allowed to run slowly into a solution of lead nitrate by means of a thread which acted as a syphon. He obtained barytes crystals similarly from ferrous sulphate and barium nitrate. The means by which mixture is brought about is of course of little importance so long as it proceeds slowly; diffusion, with or without an intervening porous membrane, has been frequently employed. Drevermann placed two powdered substances, which furnish a third insoluble substance by their interaction, in two fairly tall glass cylinders, filled each up with water and stood them both in a third larger cylinder containing water, so that the smaller cylinders were completely submerged. In the course of some months, crystals of the very sparingly soluble product of the reaction of the two soluble com-

pounds were deposited around the rims of the small cylinders; by this method crystals of crocoisite were obtained by the slow diffusion of solutions of potassium chromate and lead nitrate. Other workers have employed diffusion through a porous membrane for the purpose of obtaining crystals; the latter are, however, in this case mostly deposited on the membrane, so that towards the end of the operation the diffusion is greatly hindered. In such cases, it is found convenient to employ two porous diaphragms, arranged so that the two reacting solutions are initially separated by a layer of water. Sometimes, it is impossible to select reacting substances which are both readily dissolved by the solvent employed; if one of them is fairly soluble, the following process is often applicable. The sparingly soluble substance is put into the solution of the more soluble; the chemical change then gradually occurs, and after some weeks or months the product is deposited in crystals on the solid mass. By immersing plates of gypsum in a dilute solution of sodium bicarbonate, Becquerel caused calcite crystals to form on the solid gypsum. The same investigator also obtained a deposit of vivianite (crystalline iron phosphate) upon iron plates placed in a solution of ammonium phosphate. Operations of this kind are often hastened by being conducted at a high temperature and pressure; thus Wibel synthesized malachite by heating marble and copper sulphate with water in a closed tube at about 180° , and Becquerel obtained a series of other minerals, such as aragonite, azurite, &c., by similar means.

Many reduction processes furnish excellent examples of this kind of crystallization; most solutions of sulphates yield the corresponding metallic sulphides in a crystalline form when acted upon by organic reducing agents. A number of proto-salts, such as ferrous sulphate, stannous chloride,

&c., cause the separation of the noble metals in the crystalline form from their solutions. As is well known, certain of the heavy metals, such as bismuth and lead, are thrown down in crystals from solutions of their salts by metallic zinc.

Finally, it should be mentioned that some substances may be caused to separate from their solutions by the loss of gases. An example of this is found in the deposition of crystalline calcium carbonate from its solution in aqueous carbonic acid, by gradual loss of carbon dioxide.

IV. MOLECULAR CHANGE. Many solid substances, such as iron, silver, and arsenic anhydride, have the power of spontaneously changing from the amorphous to the crystalline form, owing to rearrangement of their molecules. Further, crystalline substances frequently change their crystalline form. Such a case is found in the change of monosymmetric sulphur crystals, obtained by solidification of the molten element, into an aggregate of orthorhombic pyramids; a change which is complete after a few days' standing. Numerous examples of this same phenomenon are met with in the province of dimorphism. Apparently such molecular change is promoted by shaking; subjection to high temperature, as well as the presence of certain liquids and gases, also exert a considerable influence on the result. Thus, at a high temperature and pressure, quartz is converted into tridymite, and limestone into granular marble.

Crystallization is often assisted by heating the amorphous substance in a stream of gas. By this method Deville and Troost obtained most of the metallic oxides in crystals; and in their experiments the nature of the gas used did not appreciably affect the result. The beautiful crystals of cassiterite obtained by heating stannic oxide in a current of hydrogen chloride, owe their formation less to molecular

change than to sublimation; since a small quantity of tin chloride is formed during the process and carries tin oxide away with it during volatilization; the oxide is then deposited in crystals on the cooler parts of the apparatus.

The action of liquids in promoting molecular change must be ascribed essentially to their solvent properties, even if no actual solution be apparent. In illustration of this may be quoted the conversion of amorphous calcium carbonate into calcite when left in contact with water, and of amorphous zinc carbonate into calamine under similar conditions; freshly precipitated mercuric sulphide also changes to cinnabar when left in contact with caustic potash solution.

V. ELECTROLYSIS. Electrolysis is but seldom applied to the preparation of artificial crystals, partly because the regular form of the individual crystals obtained is more or less spoilt by structural anomalies; partly also because the best crystals can only be grown by the application of very weak currents, much time being hence occupied. As a rule the crystals required can be prepared with much greater ease and certainty by other methods. Electrolytic methods are only used for the crystallization of a few metals. Thus, Dauber obtained a well-developed crystal of silver, consisting of the octahedron and the hexakisoctahedron, by the electrolytic decomposition of silver nitrate; copper and lead were also obtained in distinct crystals by similar means.

CHAPTER XVI.

HISTORICAL SKETCH OF ISOMORPHISM.

It has been mentioned above that Haüy stated the principle that every chemical substance possesses a characteristic crystalline form, and that substances differing in chemical composition cannot occur in the same form. This view, so soon as it became known, found general acceptance, although certain facts were known before Haüy's time, which were at variance with it. Among these is the old observation that copper and ferrous sulphates crystallize together from a solution containing them both. De l'Isle referred to this fact in 1772, and in 1784 Le Blanc showed that, whilst the chemical composition of the deposited crystals changes, their crystalline form remains the same. He also found that ordinary potash alum will take up considerable quantities of iron alum without any alteration in crystalline form. Vauquelin, in 1797, found the same relation to hold between the potash and ammonia alums, and in 1816 Gay-Lussac stated that a crystal of potash alum will grow in a solution of ammonia alum, whilst the crystalline form remains constant.

The work of Beudant possesses great importance in connexion with this subject; from a study of the mixed crystallization of the sulphates of zinc, iron, and copper, he arrived at definite conclusions as to the development of one or another form on the 'mixed crystals,' and also

ascertained with certainty that the composition of the individual crystals is not constant. Bernhardt had previously remarked that zinc sulphate separates from solution in the same form as ferrous sulphate, if a little of the latter salt be added to the solution. Beudant then showed that at least 15% of ferrous sulphate must be added before this phenomenon can occur; if less than this proportion be present, the resulting crystals retain the ordinary form of the zinc salt, though at the same time containing a noteworthy quantity of ferrous sulphate. He found also that to obtain copper sulphate in the crystalline form of ferrous sulphate, at least 9% of the latter salt must be present in the solution. The same author further stated that all the three salts mentioned above may occur in a single crystal, and that each of them will crystallize with magnesium or nickel sulphate. In order to distinguish them from chemical compounds obeying the law of constant proportions, on the one hand, and from mere mechanical mixtures, on the other, Beudant described such mixed crystals as 'chemical mixtures'; it cannot be denied that the above facts are on the whole correctly coordinated in this way. Besides Beudant, Berthollet and von Fuchs were the most important antagonists to Haüy's law. It will be easily understood that Berthollet's opposition was the greater inasmuch as he disbelieved the law that chemical compounds follow constant proportions. In this lies the explanation of his bringing forward somewhat doubtful arguments in support of his case, so that his side of the discussion has at present no particular interest.

Von Fuchs' view is best expressed in his memoir on gehlenite written in 1815. He there states that iron is not an essential constituent of this species, but merely a 'vicarious' one, taking the place of an equivalent quantity of calcium. The results of a number of analyses

of minerals must be interpreted from this point of view; otherwise the law of chemical combination in constant proportion must be disregarded, and the various mineral species will also become unnecessarily subdivided. Two years later von Fuchs discussed the similarity in crystalline form existing between the carbonates and sulphates of calcium, strontium and lead, and explained the facts by his hypothesis of so-called vicarious constituents.

Haüy, however, was in no way induced to change, or to essentially modify, his opinion by the arguments stated above, and in this course he was followed by most of his contemporaries. Contradictory observations were either denied or explained on the assumption that substances with great powers of crystallization, even when contaminated with very large quantities of foreign bodies, constrained the latter to assume their own crystalline form. The fact that two chemically distinct substances not belonging to the cubic system, can occur in the same form, was most obstinately combatted. Some of the opposing facts noted in connexion with mineralogy were explained as due to pseudomorphism, it being supposed that crystals might be altered in composition, whilst their external form was preserved unchanged, just as is seen in the petrification of wood.

In 1819, Haüy's views received official recognition by the Parisian Academy, to which Beudant's work was submitted for criticism. Haüy, and with him, Vauquelin and Brochant, assisted in passing judgment; this resulted in the statement that definite chemical compounds were known in which one of the constituents determined the form, even if it be present only in small proportion, the other constituents being without influence on the crystalline form. The importance of Beudant's work was thus wholly disregarded.

In the same year (1819), whilst the correctness of Haüy's theory was still all but universally recognized, Mitscherlich showed irrefutably that the phosphates and arsenates of potassium or ammonium possess the same crystalline form. A remodelling of the theory thus became not only necessary, but the direction which the change should take was also indicated. The honour of this most important discovery belongs entirely to Mitscherlich, and is the greater inasmuch as he then knew nothing of his predecessor's work. The discovery practically resulted from a happy accident. Mitscherlich was at this time a young man of about twenty, and this research was his first work; he had no leaning towards crystallography, and had undertaken the research upon quite other than crystallographic grounds. Berzelius had found the ratio of the amounts of oxygen present in phosphoric or arsenic acid to that in phosphorous acid to be as 5 is to 3. Mistrusting the analytical results, however, and considering this ratio to be of too complicated a character, Mitscherlich supposed it not impossible that the ratio would be established as 2 : 1 by more accurate determinations. He therefore repeated the work of Berzelius, but could only confirm the latter's results; at the same time he observed that the crystalline salts of phosphoric and arsenic acids exhibited great similarity in form. Small as was his knowledge of crystallography, he saw himself upon the eve of an important discovery, and although the problem did not belong to his original scheme of work, he sought to place the question upon a more secure basis. Under the guidance of his friend Gustav Rose he therefore studied the laws and methods of crystallography, and by means of his first measurements was enabled to complete a most fruitful portion of the whole work. The complete morphological concordance between the corresponding phosphates and

arsenates, which Mitscherlich had previously suspected from mere inspection of the external forms, was thus established. The acid phosphates and arsenates of ammonium were first studied, and then other acids were sought which, when combined with the same base, should give salts of the same crystalline form. Such acids, however, could not be found; Mitscherlich therefore investigated other bases which should combine in the same proportion. This latter condition was fulfilled by the potassium salts of phosphoric and arsenic acids, which possess the same crystalline form as the ammonium salts; this important result was of the greatest interest to Mitscherlich, as he hoped by its aid to gain some insight into the then problematical nature of ammonia.

Before publishing his discoveries, Mitscherlich considered it necessary to extend them by a further examination of artificial salts; this would enable him to oppose Haüy's views, with which he had in the meantime gained some acquaintance, not only by a few exact observations, but also by a large number of specific cases. For this purpose the sulphates and carbonates of barium, strontium, and lead were examined, and, as von Fuchs had already noted, were found to be at variance with Haüy's theory; further, the carbonates of calcium, iron, magnesium, and zinc were expected to show the same mutual relations as the arsenates and phosphates. On gaining a knowledge of the observations of Beudant, Mitscherlich repeated and completed the work of the former. It was then found that in all his investigations, Beudant had neglected to analyze the crystalline mixtures obtained; the water of crystallization had thus been completely left out of consideration, and the explanation of the phenomena observed was correspondingly imperfect.

Whilst Mitscherlich was occupied with this work—in

the autumn of 1819—Berzelius passed through Berlin on his return journey from Paris to Stockholm, and made the acquaintance of the young chemist and his investigations. Berzelius, who was then recognized as the first authority in the department of chemistry, was greatly impressed by the importance of Mitscherlich's discoveries, and arranged matters so that the latter was sent to Stockholm at the government expense, in order to complete his work and to apply himself more especially to chemistry. Berzelius was interested in the enquiry principally upon two grounds; he hoped to derive from its results an explanation of the numerous exceptions to the law of constant proportions which were met with in his chemical system of minerals, and at the same time he expected to obtain some starting-point for the determination of atomic weights. Mitscherlich's next idea was to denote his discovery by some special name. Substances, which behave towards each other like the acid arsenate and phosphate of potassium, were therefore termed isomorphous; similarly, the phenomenon of two different substances possessing the same or nearly the same crystalline form was named isomorphism.

The great influence and authority of Berzelius ensured that Mitscherlich's discovery should everywhere receive proper and immediate appreciation. Haüy alone disregarded all the convincing arguments which were brought to bear against his views. At a time when our chemical knowledge of minerals was rudimentary, Haüy had, in many cases, been able to foresee the analytical results by means of his theory. The latter had achieved a too brilliant success to allow him thus to give it up. And yet his theory was not completely invalidated by Mitscherlich's discovery, which only necessitated a fundamental reconstruction. An identity in crystalline form did not require identity in chemical composition, but analogy in

composition and constitution. Haüy, however, towards the close of a brilliant career, was not inclined to alter a principle which he erroneously considered as his greatest discovery. He held to his former views, and indeed wrote to Brochant saying that if Mitscherlich's theory were correct, Mineralogy would be the most wretched of sciences (*la science la plus pitoyable*). The opposition from this quarter did not, however, last long; Haüy died in 1821, and after his death Mitscherlich's discovery rapidly received general recognition amongst chemists¹.

¹ G. Rose, *Zeitsch. Geol. Ges.* xvi 21.

CHAPTER XVII.

THE GEOMETRICAL AND PHYSICAL PROPERTIES OF ISOMORPHOUS SUBSTANCES.

FROM the results of his early work on the phosphates, arsenates, and sulphates, Mitscherlich concluded that identity of crystalline form was not conditioned so much by the material nature of the chemical components, as by the total number and the mutual arrangement of the atoms contained in the molecule. This may at first seem somewhat strange, when it is remembered that at the very outset of his investigation, Mitscherlich discovered the isomorphous nature of potassium and ammonium ; it must not be forgotten, however, that the nature of ammonia was at this time quite misunderstood, and that Mitscherlich also had the facts of dimorphism before him, since only on this assumption are his statements intelligible. It is indeed remarkable that the non-dependence of the external form upon the nature of the atoms composing the substance was thus enunciated ; Mitscherlich himself was specially cognizant of the uncertainty of this deduction, and expressed the opinion that it might have to undergo revision. He indeed ultimately introduced the change himself. From

the phenomena presented, on the one hand, by a large number of substances (more especially by the oxides and chlorides) and, on the other, by cases of similarity in form such as is shown by the pyroxenes and amphiboles, he finally concluded that only those substances should be described as isomorphous which possess analogous chemical composition and identical crystalline forms, and crystallize together in varying proportions. This definition has remained essentially unchanged up to the present day, in spite of many attacks and attempted misinterpretations. It is therefore unnecessary to discuss further the different views which have been put forward by individual workers, more especially as they will receive mention elsewhere (Chapter XXIV). A critical review of the subject of isomorphism cannot be attempted without a previous consideration of the whole subject, and will therefore be postponed till the end of the present chapter; the above definition of isomorphism will be, on the whole, adhered to throughout the following pages.

From a purely geometrical point of view, isomorphous substances are recognized by the correspondence and similarity of their external form. This agreement in form is, however, with the exception of cubic substances, not so absolute as would be indicated by the name, but is only a more or less approximate correspondence. This fact was already known to Wollaston in 1812, as the result of exact measurements made on the carbonates and sulphates of barium, strontium, and lead with his newly invented reflecting goniometer; his observations, however, received but little attention. It was generally regarded as a consequence of Haüy's theory that a small proportion of a foreign compound, when present in a substance, lost its characteristic crystalline form and assumed that of the main bulk; the form of the latter was supposed to be quite unaffected by

the contamination. The acceptance of Wollaston's observations, and also those of Bernhardt and Weiss, was prevented in Germany by the authority of Mitscherlich, notwithstanding that the latter had himself noticed some slight angular variations on crystals of the salts investigated by him. Later on Mitscherlich was one of the first to accept Beudant's demonstration of the erroneous nature of Haüy's views, when the accuracy of Wollaston's observations had received new confirmation from Biot. At first, however, Mitscherlich was not in a position to follow up Wollaston's statements, lacking as he did the necessary apparatus; further, instruments with which angles could be accurately measured to minutes, were at that time mere curiosities, and did not quickly come into common use. Possibly also Mitscherlich did not at first credit the matter with the necessary importance; he was a chemist, interested in crystallography mainly from its chemical aspect, and only in his later years really applied himself to purely crystallographic problems.

The differences observed between the corresponding angles of isomorphous substances, vary from a few minutes up to several degrees; thus, corresponding angles measured on the various rhombohedral carbonates are given in the following table:—

Substance.	Composition.	Rhombohedron Angle.
Calcite .	CaCO_3	$74^\circ 55'$
Dolomite .	$\text{CaMg}(\text{CO}_3)_2$	$73^\circ 45'$
Magnesite .	MgCO_3	$72^\circ 40'$
Calamine .	ZnCO_3	$72^\circ 20'$
Chalybite .	FeCO_3	$73^\circ 0'$
Rhodoerosite	MnCO_3	$73^\circ 9'$

The observed differences for the orthorhombic carbonates are by no means so large:—

Substance.	Composition.	Prism Angle.	Brachydome Angle.
Aragonite . .	CaCO	63° 50'	71° 34'
Strontianite. .	SrCO ₃	62° 41'	71° 48'
Cerussite . .	PbCO ₃	62° 46'	71° 44'
Witherite . .	BaCO ₃	62° 12'	72° 16'

Naturally, no definite limits can be assigned within which the angular differences of isomorphous substances must lie; it is, in the end, more or less a matter of personal judgment whether or not a given large angular difference is, or is not, compatible with isomorphism.

The angular differences observed between isomorphous substances are generally well indicated by a comparison of the axial ratios of the crystals¹. A careful consideration of the axial ratios and angles shows, further, that when two undoubtedly isomorphous substances show a great difference in crystalline form, this difference is but seldom equally marked over the whole form. In orthorhombic, monosymmetric, or anorthic crystals, the difference between isomorphous substances is ordinarily most evident in a certain principal zone, whilst between the angles of other zones nearly perpendicular thereto, practically complete identity exists. Since the crystallographic axes generally lie parallel to the principal zones, these regularities are satisfactorily expressed by the axial ratios; two of these agree more or less completely, whilst in the third the difference is distinctly shown. The following table comprises a few examples of this kind:—

¹ See Groth's *Tabellarische Uebersicht der Mineralien*.

Substance.	Composition.	System.	Crystallographic Constants.
Selenium .	Se	monosymmetric	0.9907 : 1 : 1.2700 $\beta = 89^{\circ}15'$
Sulphur .	S	„	0.9958 : 1 : 0.9998 $\beta = 84^{\circ}14'$
Orpiment .	As ₂ S ₃	orthorhombic	0.9044 : 1 : 1.0113
Stibnite .	Sb ₂ S ₃	„	0.9844 : 1 : 1.0110
Wollastonite	CaSiO ₃	monosymmetric	1.0534 : 1 : 0.4840 $\beta = 84^{\circ}30'$
Augite .	(MgFe)(AlFe) ₂ SiO ₆	„	1.0585 : 1 : 0.5942 $\beta = 89^{\circ}38'$
Spodumene	LiAl(SiO ₃) ₂	„	1.0539 : 1 : 0.7686 $\beta = 89^{\circ}13'$

In general, the statement may be made that the correspondence in crystalline form is greater in proportion as the substances concerned are more similar in their chemical behaviour ; the similarity in form hence furnishes a measure of the isomorphism, which is, in the end, a consequence of the chemical similarity of the substances concerned.

Perhaps the most instructive series of measurements of isomorphous substances is that made by Tutton¹ on the monosymmetric double sulphates of the composition R₂SO₄, R''SO₄, 6H₂O. Each of the twenty-two salts measured contains as the metal R, one of the three alkali metals potassium, rubidium, or cæsium ; the salts may hence be arranged in series of three, containing the same dyad metal R'', but different monad ones. When this is done, as in the appended table, which gives the axial ratios and the interaxial angle β , it is seen that all the geometrical properties of the rubidium salts are intermediate between the corresponding properties of the potassium and cæsium salts. The same is also true of the

¹ *Journ. Chem. Soc.*, 1893, p. 337.

facility of crystallization and the crystalline habit assumed by the rubidium salts. The extent to which this intermediate position of the rubidium salts, between those of potassium and caesium, is a quantitative one, is indicated by the following table, which gives the differences in the

Salt.	$a : b : c.$	$\beta.$
$K_2SO_4, MgSO_4, 6H_2O$. .	0.7413 : 1 : 0.4993	75° 12'
$Rb_2SO_4, MgSO_4, 6H_2O$. .	0.7400 : 1 : 0.4975	74° 1'
$Cs_2SO_4, MgSO_4, 6H_2O$. .	0.7279 : 1 : 0.4946	72° 54'
$K_2SO_4, ZnSO_4, 6H_2O$. .	0.7413 : 1 : 0.5044	75° 12'
$Rb_2SO_4, ZnSO_4, 6H_2O$. .	0.7373 : 1 : 0.5011	74° 7'
$Cs_2SO_4, ZnSO_4, 6H_2O$. .	0.7274 : 1 : 0.4960	72° 59'
$K_2SO_4, FeSO_4, 6H_2O$. .	0.7377 : 1 : 0.5020	75° 28'
$Rb_2SO_4, FeSO_4, 6H_2O$. .	0.7377 : 1 : 0.5004	74° 16'
$Cs_2SO_4, FeSO_4, 6H_2O$. .	0.7261 : 1 : 0.4953	73° 8'
$K_2SO_4, NiSO_4, 6H_2O$. .	0.7379 : 1 : 0.5020	75° 0'
$Rb_2SO_4, NiSO_4, 6H_2O$. .	0.7350 : 1 : 0.5022	73° 57'
$Cs_2SO_4, NiSO_4, 6H_2O$. .	0.7270 : 1 : 0.4984	72° 58'
$K_2SO_4, CoSO_4, 6H_2O$. .	0.7404 : 1 : 0.5037	75° 5'
$Rb_2SO_4, CoSO_4, 6H_2O$. .	0.7391 : 1 : 0.5011	73° 59'
$Cs_2SO_4, CoSO_4, 6H_2O$. .	0.7270 : 1 : 0.4968	72° 52'
$K_2SO_4, CuSO_4, 6H_2O$. .	0.7490 : 1 : 0.5088	75° 32'
$Rb_2SO_4, CuSO_4, 6H_2O$. .	0.7490 : 1 : 0.5029	74° 42'
$Cs_2SO_4, CuSO_4, 6H_2O$. .	0.7429 : 1 : 0.4946	73° 50'

angle β between the potassium and rubidium, and the rubidium and caesium salts; for any series of three salts these two differences are seen to be identical within the limits of experimental error. Since the atomic weight of rubidium (85) is approximately the mean of those of

potassium (39), and cæsium (133), it follows that the differences between the axial angles of the potassium, rubidium, and cæsium salts are proportional to the differences in the atomic weights of those metals; this, of course, only holds if the dyad metal in the series be kept unchanged. The same kind of relationship is found between all the numerous angles measured on the crystals.

Dyad metal present.	Value of β for K salt.	Difference.	Value of β for Rb salt.	Difference.	Value of β for Cs salt.
Magnesium .	75° 12'	71'	74° 1'	67'	72° 54'
Zinc . .	75° 12'	65'	74° 7'	68'	72° 59'
Iron . .	75° 28'	72'	74° 16'	68'	73° 8'
Manganese .	—	—	74° 3'	70'	72° 53'
Nickel . .	75° 0'	63'	73° 57'	59'	72° 58'
Cobalt . .	75° 5'	66'	73° 59'	67'	72° 52'
Copper . .	75° 32'	50'	74° 42'	52'	73° 50'
Cadmium .	—	—	74° 7'	78'	72° 49'

The influence exerted on the crystalline form of these salts by a change in the dyad metal cannot be followed quantitatively; because salts containing the same alkali metal and different dyad metals, which are chemically very closely related, such as nickel and cobalt, have axial ratios and interaxial angles which, within the limits of experimental error, are almost identical. On the other hand, it would perhaps hardly be expected that a very close relationship would be traceable between the crystallographic constants of two salts which, though containing the same alkali metal, also contain dyad metals, such as copper and nickel, which are not chemically closely related. This series of measurements is of the greatest value, not only as illustrating a specific case of isomorphism, but also because it indicates the kind of relationship which will probably be found ultimately to hold generally in isomorphous series.

Early in the forties, Kopp supposed that he had found another measure of isomorphism. From his own observations and those of others, but more especially of Dumas, he concluded that the molecular volume—the molecular weight divided by the specific gravity—of isomorphous substances is the same; this correspondence is, as a rule, the greater, as the observed similarity in geometrical form is the greater. In many cases, the equality of the molecular volumes is complete, but in others the results leave much to be desired in this respect; in some few cases also, the molecular volumes stand in a simple ratio one to the other. Some examples are given in the following table:—

Substance.	Composition.	Molecular Volume.
Calcite . . .	CaCO_3	36.8
Magnesite . . .	MgCO_3	27.8
Calamine . . .	ZnCO_3	28.0
Chalybite . . .	FeCO_3	30.3
Rhodocrosite . .	MnCO_3	31.9
Aragonite . . .	CaCO_3	33.9
Strontianite . .	SrCO_3	41.1
Witherite . . .	BaCO_3	45.6
Cerussite . . .	PbCO_3	40.8
Apatite . . .	$\text{CaCl}_2, 3\text{Ca}_3(\text{PO}_4)_2$	33.0
Pyromorphite . .	$\text{PbCl}_2, 3\text{Pb}_3(\text{PO}_4)_2$	40.8
Corundum . . .	Al_2O_3	25.3
Specular Iron . .	Fe_2O_3	30.5
Barytes . . .	BaSO_4	52.1
Anglesite . . .	PbSO_4	48.1
Celestine . . .	SrSO_4	46.9

The imperfect agreement may be in many cases due to inaccurate determinations of the specific gravity; the difference noticed between aragonite and witherite, and between calcite and magnesite, however, can certainly not

be thus explained away. Such examples as these must be considered as exceptions to the rule, or else the rule must be altered, so as to include, not only substances whose molecular volumes are identical, but also those whose molecular volumes are in some simple ratio; in the cases mentioned above this ratio is 3 : 4.

Subsequently to Kopp, Schröder¹ and Schrauf² studied the molecular relations between isomorphous substances without, however, materially increasing our knowledge of the subject. Mitscherlich considered the first condition of isomorphism to be that the substances concerned should contain the same number of atoms in the molecule, and should be substances of the same type; later workers have endeavoured to show that isomorphism is conditioned by equality of the molecular volumes. On the other hand, apart from exceptions of the kind quoted above, the converse of Kopp's principle does not hold. A large number of instances might be quoted, of substances which in crystallographic and chemical respects have nothing in common, but which nevertheless have the same molecular volume.

It is therefore concluded, that in the large majority of cases isomorphous substances do not possess identical molecular volumes; Muthmann³ has, however, recently shown that very important results may be expected from combining the molecular volumes with the axial ratios. As already stated, the physical molecules or structural units of a crystalline substance must be regarded as composed of several chemical molecules. In crystals of isomorphous substances, these physical molecules necessarily consist of the same number of chemical molecules, and both physical and chemical molecules are similarly arranged in the various members of an isomorphous series. Certain

¹ *Pogg. Ann.* cvii. 126.

² *Ibid.* cxxxiv. 117.

³ *Zeitsch. f. Kryst.* 1894, xxii. 497.

volumes of two isomorphous substances can hence be chosen, such that each contains the same number either of physical or of chemical molecules; these volumes are obviously proportional to the molecular volumes.

Consider now a series of isomorphous, orthorhombic substances; if in each member of such a series a volume proportional to the molecular volume be chosen, these volumes will contain the same numbers of structural units and of chemical molecules respectively. Further, suppose these particular volumes selected in the crystals to take the form of rectangular parallelepipeda, whose edges are coincident in direction with, and proportional in length to, the three rectangular axes of the crystal. The lengths of the sides of these parallelepipeda will be proportional to the distances between contiguous structural units in the various members of the series; these lengths χ , ψ , and ω can be readily calculated from the axial ratios $a : b : c$ of the crystal and its molecular volume M .

For, by the nature of the problem, the following two equations hold:—

$$\chi : \psi : \omega = a : b : c \text{ or } \frac{\chi}{a} = \frac{\psi}{b} = \frac{\omega}{c}. \quad . \quad . \quad . \quad (1)$$

and

$$M = \chi\psi\omega. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Substituting in (2) values derived from (1), it is seen that

$$M = \frac{bc\chi^3}{a^2} = \frac{ac\psi^3}{b^2} = \frac{ab\omega^3}{c^2},$$

therefore

$$\chi = \sqrt[3]{\frac{a^2M}{bc}}; \quad \psi = \sqrt[3]{\frac{b^2M}{ac}}; \quad \omega = \sqrt[3]{\frac{c^2M}{ab}}.$$

Now the length b in a set of axial ratios is always taken as unity; the ratio $a : b : c$ is consequently of the form

$a : 1 : c$. The equations for obtaining χ , ψ and ω therefore become:—

$$\chi = \sqrt[3]{\frac{a^2 M}{c}}; \quad \psi = \sqrt[3]{\frac{M}{ac}}; \quad \omega = \sqrt[3]{\frac{c^2 M}{a}}.$$

These formulæ, of course, only hold in the case of orthorhombic crystals; for monosymmetric or anorthic crystals slightly more complicated expressions are obtained, whilst for cubic or tetragonal crystals the formulæ require simplification. The values of χ , ψ and ω are termed by Muthmann the topic or topical axial ratios, and by Tutton¹ the distance ratios. As stated above, they represent the distances between the centres of adjacent physical molecules or structural units in the three axial directions, and in such a way as to allow of a strict comparison being instituted between the topic ratios of the various members of an isomorphous series.

It is instructive to consider the topic axial ratios of a crystallographically simple isomorphous series such as that of the tetragonal arsenates and phosphates of potassium and ammonium. The values of a and b in the axial ratio $a : b : c$ being both equal to unity in the case of a tetragonal crystal, χ and ψ are equal; only χ and ω therefore need be considered.

Salt.	Mol. Vol. M.	$a : c$.	χ .	ω .
KH_2PO_4 . .	58.246	1 : 0.6640	3.1419	2.9503
KH_2AsO_4 . .	62.822	1 : 0.6633	3.2232	3.0235
$\text{NH}_4\text{H}_2\text{PO}_4$. .	64.170	1 : 0.7124	3.1698	3.1934
$\text{NH}_4\text{H}_2\text{AsO}_4$. .	68.842	1 : 0.7096	3.2491	3.2606

A little consideration of these topic axial ratios leads to the following conclusions:—(1) on replacing the phosphorus atom in one of the above phosphates by arsenic,

¹ *Journ. Chem. Soc.* 1894, 628.

the distances between contiguous physical molecules are increased to the same extent in all directions; (2) this increase is approximately the same in both ammonium and potassium phosphate; (3) if the potassium atom in either potassium arsenate or phosphate be replaced by an ammonium group, the distances between the consecutive molecules are increased, but to a much greater extent in the direction of the *c*-axis than in that of the *a*-axis.

Muthmann founds on these conclusions some interesting speculations respecting the composition of the physical molecule or structural unit; he considers that the facts can only be accounted for on the assumption that the crystalline molecule of these phosphates and arsenates is composed of eight chemical molecules.

Although the topic axial ratios of only three small series of isomorphous substances have been determined up to the present, yet it may safely be predicted that conclusions of considerable importance will result from their further investigation.

As is well known, the external form of a crystal is intimately connected with its cleavage, and it is therefore not surprising that isomorphous substances should show a close analogy in respect to the latter property. This fact deserves some attention, inasmuch as the cleavage affords a definite test for isomorphism amongst cubic crystals. As an instance of identity of the cleavage form, the rhombohedral carbonates of calcium, magnesium, zinc, iron, and manganese may be mentioned; these substances are all characterized by a very perfect cleavage parallel to the primary rhombohedron. Further, the isomorphous orthorhombic sulphates of magnesium, zinc, and nickel, all show a perfect cleavage parallel to the brachydome. The agreement in the cleavage planes is not so good amongst the orthorhombic carbonates :—

Substance.	Composition.	Cleavage.	
		Perfect.	Imperfect.
Aragonite . .	CaCO_3	(010)	(110), (011)
Strontianite . .	SrCO_3	(110)	(012), (010)
Cerussite . .	PbCO_3	(110)	(010), (011)
Witherite . .	BaCO_3	(010)	(110), (012)

Jannettaz ¹ has investigated the thermal conductivity of isomorphous compounds; his results show that the analogy between the heat conductivities of such substances is just as close as is observed in the property of cleavage. The three rectangular directions of maximum, minimum, and an intermediate velocity of heat conduction in a crystalline medium are described as the axes of thermal conductivity; the latter not only occupy corresponding positions in isomorphous crystals, but their magnitudes are also in similar ratio to each other.

At present too little is known of the coefficients of expansion of crystals to allow of the deduction of any general conclusions. The results of a few observations are, however, given in the following table; α_e and α_o represent the principal coefficients of expansion for uniaxial crystals, whilst α_a , α_b and α_c are the corresponding values for biaxial crystals. A is the coefficient of cubical expansion:—

	α_e	α_o	A
Calcite	0.000310	0.00263	0.00201
Chalybite	0.000539	0.00161	0.00269

	α_a	α_b	α_c	A
Barytes	0.00143	0.00225	0.00149	0.00519
Celestine	0.00192	0.00185	0.00149	0.00526

So far as can be concluded from the above data, no close

¹ *Compt. Rend.* lxxv. 1501.

connexion exists between the coefficients of thermal expansion of isomorphous substances.

Lastly, the external form of crystals and the etched figures which may be produced on their faces are very nearly related one to the other; Baumhauer has therefore endeavoured to employ the latter property as a criterion of isomorphism. His work, however, shows that although such substances do, as a rule, give the same etched figures, yet essential differences often occur between them, more especially with respect to their position. Thus, by etching a cleavage rhombohedron of calcite with hydrochloric acid, equilateral triangular cavities, the vertices of which point towards the principal axis, are engraved; the isomorphous mineral chalybite, when treated similarly, shows similar equilateral triangular etched figures, but turned through 180° from those of calcite. Similar observations have also been made on other substances, so that no peculiar interest attaches to etched figures as a means of detecting isomorphism.

The optical characters of isomorphous substances have been more completely investigated than any other properties. Senarmont¹ first paid careful attention to this subject, and since his time Topsøe and Christiansen² have furnished important contributions to our knowledge. The results obtained by these observers, however, have not led to the deduction of any general law, although isomorphous substances, as a rule, show analogies in their optical properties, more especially when the crystals are uniaxial. Thus, in the tetragonal phosphates and arsenates of potassium and ammonium, the extraordinary index of refraction is always smaller than the ordinary one, but no equal differences between them or any analogous relation has been observed.

¹ *Ann. de Chim. et de Phys.* iii.33, 391.

² *Ibid.* v. 1, 5.

The hexagonal trapezohedral tetartohedral thiosulphates of strontium and lead have not even the same sign of double refraction, the former compound being optically negative, and the latter positive, in sign.

Biaxial isomorphous substances usually show a correspondence between the magnitudes of the principal indices; exceptions are, however, more frequent than amongst uniaxial substances. Sodium potassium dextrotartrate (seignette salt) is orthorhombic and sphenoidally hemihedral, and the double refraction is positive; the brachypinakoid is the optic axial plane, and the axis a is coincident with the first mean line. The isomorphous sodium ammonium tartrate, however, shows negative double refraction; the plane of the optic axes is parallel to the macropinakoid, and the c -axis is the first mean line. Similar differences are also to be observed between the orthorhombic sulphates and chromates of potassium and ammonium.

An even greater lack of similarity in respect to optical properties is usually noted in the case of isomorphous substances crystallizing in the monosymmetric and anorthic systems; the reason of this is, however, evident, since the orientation of the wave surface is not defined by the geometrical symmetry, as in the case of orthorhombic crystals. Although no complete investigation of the matter has been made, yet the above statement is amply justified by the work of Tschermak on augite and that of Schuster on the plagioclases.

Tutton's measurements¹ of the three principal indices of refraction of the orthorhombic sulphates of potassium, rubidium, and cesium for the sodium line D , are given in the following table in order to illustrate the kind of relation observed between the indices of refraction of isomorphous substances.

¹ *Journ. Chem. Soc.* 1894, 628.

K_2SO_4	1.4947	1.4935	1.4973
Rb_2SO_4	1.5144	1.5131	1.5133
Cs_2SO_4	1.5662	1.5644	1.5598

Although no close relationship can be observed between the indices of refraction of the three salts, yet it will be seen that the refractive indices of rubidium sulphate, the molecular weight of which lies between those of the other two salts, are intermediate between the corresponding indices of potassium and caesium sulphates.

Very little attention has hitherto been paid to the comparative study of other physical properties of isomorphous substances; those relations, however, which have up to the present been discovered and are mentioned above, satisfactorily demonstrate that isomorphism does not solely consist in similarity of external form, but also implies a greater or less correspondence between the collective properties of the substances concerned.

The generally recognized theory of the structure of crystals given in the introduction affords a basis upon which a clear conception of the nature of isomorphism may be founded. Isomorphism, as Sohncke first stated, depends on the identity of regular arrangement of the smallest particles in the substances concerned:—*two crystalline substances are described as isomorphous when they possess congruent or approximately congruent forms of structure*; a form of structure being understood to mean one of the regular infinite point systems which up to the present are recognized as possible. This definition of isomorphism is not in direct contradiction with any of those previously mentioned, and further possesses the merit of summarizing several of them.

A considerable number of substances of chemically analogous composition are known, which, whilst forming

isomorphous mixtures and exhibiting great similarity with respect to the crystalline form and the values of corresponding angles, yet belong to different crystalline systems. Amongst these may be mentioned cupro-uranite and calco-uranite, beryllium sulphate and selenate, and the felspars. Most authors only describe compounds as isomorphous if they crystallize in the same system, others, however, apply the term in a somewhat wider sense. The difference between these views loses considerably in importance if the definition of isomorphism just given is accepted, since there may be many point systems, which, although really characterized by very slight, or even no symmetry, can approximate to a higher symmetry, and may thereby simulate point systems which really possess such higher symmetry. Structural forms of this kind can be regarded as limiting forms which lie near the boundary between two crystalline systems; an explanation is thus afforded of the remarkable properties of the substances mentioned above.

The superiority of Sohncke's definition consists principally in the fact that it does not select any special property of isomorphous substances as a characteristic one; it is based upon the collective physical and geometrical properties of the substances concerned, whilst, in the end, all other definitions, without exception, depend more or less upon a 'parcelling out' of the property of isomorphism.

CHAPTER XVIII.

THE CHEMICAL PROPERTIES OF ISOMORPHOUS SUBSTANCES.

SINCE the formation of a crystal is brought about by the symmetrical arrangement of its smallest particles, the process of crystallization is a purely physical one; before speaking of the chemical properties of isomorphous bodies some few explanatory remarks on the physical side of the question are therefore necessary. It will not be denied that the arrangement of the crystalline elements is ultimately conditioned by the nature of the material of which they consist, and must therefore be deducible from a knowledge of the latter; although the discovery of this connexion is probably still a somewhat remote one. The one essential property of isomorphous substances is usually considered to be their power of co-operating in the formation of a homogeneous 'mixed crystal.' If this process of crystallizing together simply consists in a uniform arrangement of different structural units, it can hardly be described as of a chemical nature. There is, however, another mode of regarding the process; it is possible to conceive that the chemical molecules of the isomorphous substances combine together, either in the saturated solution or at the moment of separation, to form larger crystal molecules, and that the crystal is subsequently built up from such similar units. Under these conditions we have to deal with an essentially chemical process similar to that which occurs

in the crystallization of a double salt. Which of these hypotheses is correct can naturally only be determined from experimental facts. Unfortunately, however, there is still a sad lack of investigations on this subject, and a method for determining the size of crystal molecules has yet to be devised. In the older investigations the composition of the solution from which the mixed crystals separate, was not properly considered; and the obscurity surrounding the subject was still further increased by the want of a theory, giving a definite grasp of the subject, and indicating the lines on which experiments should be conducted. The invaluable work of Bakhuis Roozeboom¹, who applies thermodynamical principles to the mixed crystallization of isomorphous substances, has, however, completely changed this position.

At the outset it is premised, that the property of mixed crystallization possessed by isomorphous substances is a complete one, i. e. the mutual penetration of the molecules of the salts is the same as that which occurs in liquid solutions; it can then be shown that if equilibrium is to exist at constant temperature and pressure, a definite composition of the solution must correspond to every proportion in which mixed salts separate from it. Considering this result as established, the conditions of equilibrium between the mixed crystals and the solution can be deduced in a manner similar to that which Konowaloff applied to the evaporation of liquid mixtures. For this purpose let it be supposed that the vessel *G* (Fig. 1), which is fitted at the top with a movable piston *S*, possesses semi-permeable sides, that is, sides which, whilst allowing of the passage of water, prevent the passage of a salt dissolved in it. Water and an excess of two isomorphous substances *A* and *B* are placed in the vessel *G*,

¹ *Zeitsch. f. physik. Chem.* viii. 504.

which is then placed in water at a constant temperature, the contents of the vessel and the water bath being under

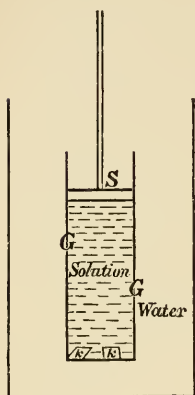


Fig. 1.

atmospheric pressure; under these conditions equilibrium may be supposed to be established between the crystalline mixture k , and the solution in which the salts A and B are dissolved. Let p_1 be the osmotic pressure set up by the dissolved salt A , and p_2 that due to the salt B , then the total osmotic pressure exerted in the vessel G has the value $P = p_1 + p_2$; equilibrium can only exist when the piston S is stationary or is loaded to an extent just sufficient to resist the osmotic pressure without being itself forced up. If the equilibrium between the mixed crystals is to be a *stable* one, any slight temporary change in the conditions must be followed by a spontaneous return to the initial conditions. Such changes may be brought about by raising or depressing the piston S . If it be raised, water will enter through the semi-permeable walls and a portion of the solid mixed crystals will consequently dissolve. If, on the other hand, the piston be pushed down, water will be forced out, and a separation of salt must occur. Now, if the relative proportions of the mixed salts A and B are the same in the solution as in the mixed crystals underneath it, then raising or lowering the piston will cause no alteration in the composition of the solution; consequently the osmotic pressure P in the vessel will not change. Under these circumstances the equilibrium is characterized as *labile*; the piston S , loaded to resist a constant pressure, will obviously remain in any position in which it is placed.

The result is, however, quite different if the composition of the mixed salts in solution is not the same as that of the solid mixture. Let c_1 be the number of molecules of the salt A contained in unit volume of the solution, and let p_1 be the partial osmotic pressure due to it; the corresponding values for the salt B may be denoted by c_2 and p_2 respectively. The proportion, y , of the salt B contained in the dissolved mixture is now :—

$$y = \frac{c_2}{c_1 + c_2}.$$

Let

$$x = \frac{c_2'}{c_1' + c_2'}$$

represent the ratio in which the same salt B is present in the underlying crystalline mixture. If x and y change, the relation holding between them will be as follows :—if x becomes smaller by solution or deposition of mixed crystals, y will necessarily increase in magnitude, and *vice versa*.

The conditions of stable equilibrium between the crystalline mixture and the solution may be formulated as follows :—

- a. *If the piston be raised.* The solution of part of the solid mixture by the water entering through the semi-permeable sides will cause the osmotic pressure P to decrease, because only in that event can the piston, which is loaded to resist a constant pressure, force out the water taken in and return to its initial position. The equilibrium is thus stable. The decrease in the osmotic pressure P may occur in two ways :—(1) by y diminishing and x consequently increasing, or (2) by y increasing and x diminishing.
- b. *If the piston be depressed.* The osmotic pressure P must increase owing to the deposition of solid matter

- consequent on the expulsion of water from the vessel; the piston will otherwise be unable to return unaided to its original position. The requisite increase in the osmotic pressure may in this case also be brought about in two ways:—(1) by an increase in y and a corresponding decrease in x , or (2) by a diminution in y accompanied by an increase in x .

It is at once seen that the conditions in the two cases can be simplified. For when x becomes smaller by solution of solid (raising the piston), and greater by deposition of crystals (lowering the piston), the relation, $y > x$, must hold; that is to say, the quantity of salt B compared to that of salt A must be greater in the solution than in the crystalline mixture. If x increases when solution occurs and decreases on deposition of solid, the relation, $y < x$, holds; i. e. the quantity of the salt B compared to that of A is greater in the case of the solid mixture than in that of the liquid. The general law governing the equilibrium between the crystalline mixture and the solution may thus be stated as follows:—*if the osmotic pressure P rises when x increases and y consequently decreases, the relation $y > x$ holds, whilst if the reverse is true then y is less than x ; or:—if the osmotic pressure of a saturated solution of a crystalline mixture increases or diminishes whilst the solid mixture under the solution becomes comparatively richer in one constituent, then the ratio of the quantity of this constituent to that of the other in the liquid must be greater or less respectively than in the solid mixture.*

Naturally, it is in general of no consequence to which salt A or B the ratios x and y refer. For the sake of convenience they will be considered as referring to B in the following pages; with addition of the further condition that B shall be that salt whose saturated solution exerts the

greatest osmotic pressure. The possible cases which may occur in connexion with solutions of two isomorphous salts may now be at once deduced from the general law stated above. These cases may be conveniently divided into two groups, according as the crystalline mixtures can exist in all proportions or only between fixed limits.

(a) *The isomorphous substances A and B mix in all proportions.* If the compounds *A* and *B* form mixed crystals in all proportions, the osmotic pressure of their saturated solution is naturally a continuous function of *x*. A curve representing the osmotic pressure as a function of *x*, may be drawn by plotting the osmotic pressures *P*, as ordinates, and the corresponding values of *x* as abscissæ. When $x = 0$, the osmotic pressure p_1° of a saturated solution of *A* is obtained, and when $x = 100$, the pressure p_2° of a saturated solution of the substance *B*; from the definition of *A* and *B*, the relation $p_2^\circ > p_1^\circ$ holds. The curve connecting these co-ordinates may now assume three forms:—It may rise continuously (Fig. 2, *I*), or

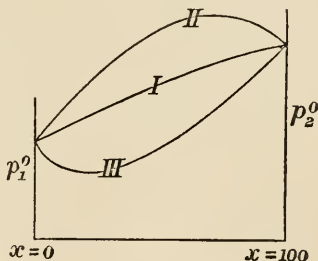


Fig. 2.

may show a maximum (Fig. 2, *II*), or a minimum (Fig. 2, *III*).

Case 1. If the curve rises continuously throughout its whole length, that is, if the osmotic pressure rises uninterruptedly as *x* increases, the relation $y > x$ will always hold, the dissolved matter always containing a greater proportion of the substance *B* than the crystalline mixture. The relation of *x* to *y* is represented graphically (Fig. 3) by taking *x* as the abscissa, and *y* as the ordinate; the curve *oaN* is thus obtained. It lies completely above the straight line which starts from

the origin and makes an angle of 45° with the two axes; on this straight line the relation $x = y$ holds.

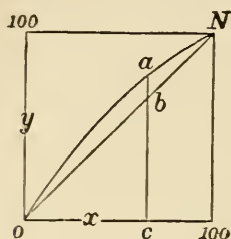


Fig. 3.

It may readily be seen from the curve oaN how the equilibrium changes as removal of the solvent by evaporation or diffusion causes a separation of the substances A and B . Let the composition of the solution corresponding to any point a on the curve be $y = ac$; as soon as evaporation commences a crystalline mixture of the composition $x = oc = bc$ separates. The composition y of the residual solution has now assumed some other value greater than ac ; this greater value of y in turn corresponds to an increased value of x . Or, as the solution evaporates, the successive separations of the crystalline mixture contain constantly increasing quantities of that constituent B , which in solution exerts the greatest osmotic pressure. A pure solution of the constituent B in contact with, and depositing, the pure substance B , would thus ultimately be obtained.

The behaviour of a mixture of alcohol and water on evaporation is perfectly analogous to this.

Case 2. The curve of osmotic pressures (Fig. 2, *II*) first rises to a maximum and then falls. Whilst the curve rises, or whilst the osmotic pressure increases as x increases, the general relation, $y > x$, holds; this, however, changes to $y < x$, when the curve falls. At the maximum point $y = x$, and the solution in which the osmotic pressure is a maximum contains the two components in the same ratio as the mixed crystals which are in equilibrium with it. The relation between x and y is shown in the same way as in case 1 by the curve $obacN$ (Fig. 4). Those values of y which are greater than the corresponding

values of x , lie on the curve oba ; those which are less than the values of x lie on the part acN .

On evaporating a solution whose y -value corresponds to ad , crystals of the same composition separate (since $y = x$); the solution thus remains of constant composition and therefore behaves just as though it contained only a single substance. If a solution whose composition corresponds to a point b on the branch oba of the curve be allowed to evaporate, a crystalline mixture of the composition of $f = cf < bf$ will separate. The

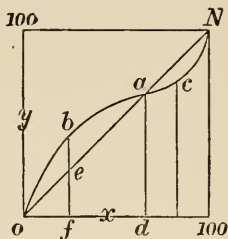


Fig. 4.

residual solution now has a greater y -value than before; its composition and that of the deposited crystalline mixture change continuously and attain the values at the point a . On the other hand, the y -value of solutions which correspond to points on the branch acN of the curve, constantly decrease, until finally the composition at the point a is attained.

Thus, if solutions whose osmotic pressure curve shows a maximum be evaporated at a constant temperature, the composition of the separating crystals continually changes in one direction, until the composition corresponding to the maximum point is attained; when this stage is reached, further evaporation does not cause the composition to change, both that of the solution and that of the mixture deposited remaining equal and constant.

The behaviour of a mixture of formic acid and water on evaporation is typical of this case; a mixture is ultimately obtained, which cannot be further resolved by distillation and behaves just like a pure substance.

Case 3. There is a minimum point on the osmotic pressure curve (Fig. 2, III). The relation between x and y

is expressed graphically by the curve oaN (Fig. 5). Analogously to case 2, it can be shown that the only solution

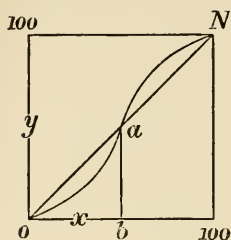


Fig. 5.

unaffected in composition by evaporation, is that which has the minimum osmotic pressure, the crystals which separate from such a solution being of the same composition as the mixture in solution. Any other solution, whose osmotic pressure lies on either side of the minimum, changes its composition on evaporation until a pure solution of A or B is ultimately obtained; whether a solution of A or of B thus results depends on whether the y -value of the original solution is less or greater than that corresponding to the minimum osmotic pressure. As evaporation proceeds, the composition of the deposited crystals becomes more and more removed from the value ob , until at length only one or the other pure substance is deposited.

The final result of the above three cases is, therefore, that by continuous separation of crystals from a mixed solution the composition (y) of the latter so changes that the osmotic pressure becomes greater and greater. If the osmotic pressure were directly proportional to the concentration of the solution, the value of the latter, $c_1 + c_2$, could be at once substituted for that of the total osmotic pressure $P = p_1 + p_2$. This, however, certainly does not always hold for the more concentrated solutions, for the osmotic pressure is directly proportional to the number of molecules present in the solution, and the number of molecules includes that of the smaller molecules (ions) produced from the chemical ones by dissociation. Since the extent of the electrolytic dissociation of the substances A and B into their ions is in general not the same, the greatest osmotic pressure

would not necessarily be exerted in the solution of greatest total concentration. The results obtained, however, may be always approximately expressed as follows:—the successive crops of mixed crystals which separate on evaporating a mixed solution, continuously alter in such a way as to contain the most soluble constituent, or most soluble mixture of the two constituents, in larger and larger proportion. In case 1, the substance *B* is the most readily soluble *phase* in the system; in case 2, a definite mixture is more soluble than either *A* or *B*, whilst in case 3, either the substance *A* or *B* acts as the most soluble, since either is more easily dissolved than any mixture of the two.

In order to follow continuously the separation which attends removal of the solvent, a converse method of consideration to the above may be adopted; what will happen if crystalline mixtures be brought in contact with successive quantities of fresh, pure solvent? In case 1, the least soluble component *A* will ultimately remain undissolved; in case 2, one or other constituent will remain, according as the *y*-value of the resulting solution is less or greater than that corresponding to the maximum osmotic pressure. Conversely, in case 3, that mixture will ultimately remain which is in equilibrium with the saturated solution of minimum osmotic pressure.

(*b*) *The substances A and B only form solid solutions¹ between certain definite limits.* If the compounds *A* and *B* are only miscible within certain limits, they will behave similarly to such partially miscible liquids as ether and water. Ether and water are mutually soluble only within

¹ The term 'solid solution' was first applied by van't Hoff to isomorphous mixtures; such solid mixtures have much in common with liquid and gaseous solutions.

certain definite limits; the two saturated solutions of the one in the other are characterized by the possession of equal vapour tensions, since otherwise they could not be in equilibrium with each other. Consequently, the two kinds of mixed crystals yielded by the partially miscible substances *A* and *B* must correspond to the same osmotic pressure; otherwise they could not be in equilibrium with the same solution. But, according to Gibbs' phase rules, the composition of the solution is quite independent of the ratio of the quantities in which the two kinds of crystalline mixtures are present beneath the solution; because there then exist three phases (solution, and two kinds of crystals). And since only three substances (solvent, *A*, and *B*) are present, the equilibrium is completely determined at a fixed temperature and under a constant pressure (1 atmosphere); the composition of the solution, and therefore also the osmotic pressure, are hence constant.

In this case then the osmotic pressure of the saturated solution cannot be a continuous function of the composition (x) of the mixed crystals. The ends of the two branches of the curve representing the osmotic pressure as a function of x , will be joined by a line parallel to the

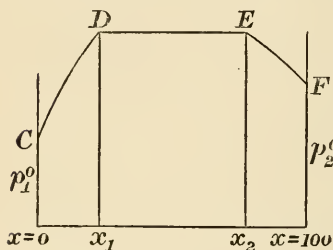


Fig. 6.

abscissæ; the end points of this straight line will thus correspond to the limiting values x_1 and x_2 , between which no crystalline mixtures are possible. The osmotic pressure curve from these end points, up to those representing the pressures of the pure saturated solutions of *A* and

B, can follow different paths which are considered below.

Case 4. One of the possible cases is illustrated graphi-

cally by Fig. 6. The osmotic pressure of that solution which is in equilibrium with the two kinds of mixed crystals is here represented as having a maximum value. On the rising part CD of the curve, y is greater than x , i. e., the solution is richer in the most soluble substance B than is the solid; conversely, in the branch EF of the curve, y is less than x . Consequently, the y -value of the solution which is in equilibrium with both kinds of mixed crystals, must be at once greater than x_1 and less than x_2 ; x_1 and x_2 representing the compositions of the limiting crystalline mixtures. The relation between x and y is represented as before by the curves oD and EN (Fig. 7) joined by the straight line DGE . From this it is seen, that by the evaporation of a solution whose composition corresponds to any point on oD , the composition changes until it attains the value at the point D ; and conversely,

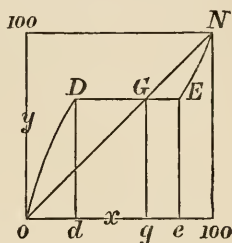


Fig. 7.

any solution corresponding to a point on EN , in the end reaches the composition at the point E . The composition of the crystals which separate, naturally changes in a reciprocal manner, tending always towards the first (x_1) or the second (x_2) ratio of mixture. When the solution has attained the y -value $Dd = Ee$, its composition cannot again alter; and by further evaporation, the second kind of limiting crystals always separates, since the y -value of the solution lies between the x -values ($x_1 = od$ and $x_2 = oe$) of these two kinds of crystalline mixtures. Crystallization from such a solution seems to occur henceforth as from a simple solution, and the two kinds of limiting crystals are always obtained ultimately from solutions of any composition. The relations holding in a mixture of butyl alcohol and water are of a nature completely analogous to this.

Case 5. Another possible case is illustrated by Fig. 8.

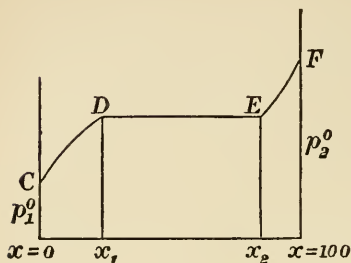


Fig. 8.

and E are thus greater than x_1 and x_2 . The relation between y and x is shown by the curve $oDEN$ (Fig. 9) which lies wholly above the straight line oN .

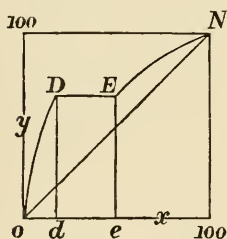


Fig. 9.

By evaporating a solution corresponding to this case, its composition, y , will constantly change in the direction from o to N . On evaporating a solution containing a relatively small proportion of the most soluble constituent B , in which consequently y has a small value, y will move along the curve oD and the x -value of the deposited crystals will continually increase until the solution and the crystals attain the respective values x and y of the point D . At this instant, the composition of the crystals suddenly increases from $x_1 = od$ to $x_2 = oe$. So long, however, as both the limiting kinds of mixed crystals are in contact with the solution, the latter must have the constant composition y ; since now $y > x_2 > x_1$, this is only possible, if the dissolved solid which should separate on further evaporation, changes a crystalline mixture of the composition x_1 already deposited into a solid mixture of the composition x_2 . Until this change is quite complete, the solution remains of constant

The osmotic pressure of the solution which is in equilibrium with both kinds of mixed crystals, lies between those of the solutions of the two components A and B ; the two side branches CD and EF of the curve rise, and the y -values of the points D

wholly above the straight line oN . By evaporating a solution corresponding to this case, its composition, y , will constantly change in the direction from o to N . On evaporating a solution containing a relatively small proportion of the most soluble constituent B , in which consequently y has a small value, y will

composition; when, however, the first kind of mixed crystals is wholly replaced by the second, the y -value of the solution can change further from that of the point E to that of N , and simultaneously the x -value of the crystals increases from x_2 to 100.

In case 4 the solution ultimately attains a certain composition which is then preserved unchanged during evaporation to complete dryness; in case 5, however, this constancy of composition is only temporary. Further, the crystals separating during the final stage of case 4, taken as a whole, have always the same average composition, although consisting of two kinds; this behaviour, however, is not exhibited in case 5, even though the solution may remain constant in composition for a time.

The question now arises, whether other cases than those discussed above can be distinguished. It might perhaps be supposed that the osmotic pressure of the solution corresponding to the two limiting species of mixed crystals, which is taken as a maximum in case 4, might also be taken as a minimum, as was done in connexion with the former continuous series of mixtures. A little reflection, however, shows that such a case is an impossible one. The line DE in Fig. 6 would then have to lie below the points C and F , and of the two terminal branches of the curve, CD and EF , the former would fall and the latter rise; therefore at the point D the relation, $y < x_1$, would hold, whilst at E the converse, $y > x_2$, would be true. But both the y -values are equal and x_2 is greater than x_1 ; this case therefore cannot occur. The direction of the side branches which are connected by the straight line DE must consequently be, in general, either as represented in Fig. 6 or Fig. 8. It is, of course, not impossible that cases might arise in which these side branches of continuous curvature might also show points of maxima or minima. In Fig. 6 minimum

points might occur on both branches, whilst in Fig. 8 a minimum might be present on the branch *CD* and a maximum on *EF*. Such cases would simply be combinations of cases 4 with 3, and of 5 with 2 or 3 respectively.

The theory of the mixed crystallization of, or the formation of solid solutions by, isomorphous substances is thus formally and clearly enunciated, so far as constant temperature is concerned. No experiments respecting the influence of temperature changes have yet been made; it is to be expected, however, that if solid mixtures are formed with absorption of heat, the miscibility will decrease as the temperature rises.

So far as the facts already observed in connection with isomorphism are any guide, it would seem that examples of case 1 are not infrequent. Thus, the sulphates of nickel, magnesium, and zinc form mixtures in all proportions containing seven molecules of water of crystallization; in such mixtures, further, the most soluble constituent ultimately completely replaces the less soluble ones. On the other hand, substances which mix in all proportions and give a certain mixed solution which possesses maximum or minimum osmotic pressure, are at present not known with any certainty. It may be expected, however, that such cases would occur amongst those substances which are not only completely miscible but also form double salts; certain salts of silver and sodium, and of magnesium and calcium behave thus. Any particular example can only be quoted as typical of one or another case after both the mixed crystals and the solutions in equilibrium with them have been analyzed; the solutions have unfortunately been totally ignored up to the present. One example of case 4 was, however, completely investigated by Bakhuis Roozeboom¹; this instance deals with mixtures of the chlorates of

¹ *Zeitsch. f. physik. Chem.* viii. 531.

potassium and thallium. Both these substances crystallize in the monosymmetric system, possess similar crystalline forms, and give rise to isomorphous mixtures, not, however, in all proportions. The following table gives the experimental results:—

Number of experiment.	One litre of Solution contains				$c_1 + c_2$.	$y = \frac{c_2}{c_1 + c_2}$.	Molecular percentage of KClO_3 in the mixed crystals x .
	grams of		milligram molecules of				
	TiClO_3 .	KClO_3 .	TiClO_3 c_1 .	KClO_3 c_2 .			
I	25.637	—	89.14	—	89.14	0	0
2	19.637	6.884	68.27	56.15	124.42	45.13	2.00
3	12.001	26.100	41.73	212.89	254.62	83.61	12.61
4	9.036	40.064	31.42	326.79	358.21	91.23	25.01
5	7.885	46.497	27.42	379.26	406.68	93.26	36.30 and 97.93
6	7.935	46.535	27.60	379.57	407.17	93.22	
7	6.706	46.410	23.32	378.55	401.87	94.20	99.28
8	6.723	47.109	23.37	384.25	407.62	94.27	99.60
9	4.858	47.312	16.89	385.91	402.80	95.81	99.62
10	2.769	47.134	9.63	384.46	394.09	97.56	99.67
11	—	49.925	—	407.22	407.22	100	100

Experiments 1 and 11 were made with solutions of the pure salts. The mixtures deposited in experiments 7–10 were scale-shaped crystals similar in appearance to those of potassium chlorate; experiments 2–4 yielded much smaller, acicular crystals resembling those of thallium chlorate. Both kinds of crystals were obtained side by side in experiment 5; after removing them, and allowing the mother liquor to evaporate, the same two kinds of crystals separated and the solution preserved its composition unchanged, as is shown by No. 6. Such behaviour is, however, only possible if the deposited crystals have the same average composition as the dissolved matter. This is confirmed by analysis, the crystals containing 93.8 per cent of potassium chlorate and the solid matter in solution 93.22; the slight difference is, of course, to be ascribed to experimental error.

The mother liquor from experiment 6 was again allowed to evaporate and the deposited crystals were then carefully sorted into the two kinds and analysed. The percentages of potassium chlorate thus obtained were respectively 36.3 and 97.93.

On representing graphically the relation between x and y in this example, a curve is obtained which is completely analogous to Fig. 7; it shows $od=x_1=36.3$, $Dd=Ee=93.24$, $oe=x_2=97.93$. There is a very large gap in the series of mixtures reaching from 36.3 to 98 per cent. of potassium chlorate. The straight line DE is thus very long; it also lies very high on the curve, inasmuch as the solution which is in equilibrium with both kinds of mixed crystals contains much more potassium chlorate than thallium chlorate ($y=93.24$). The first kind of mixed crystals (0-36.3 per cent potassium chlorate) is deposited from solutions whose dissolved substance is much richer in potassium chlorate; the branch CD (Fig. 6) consequently rises very rapidly. The second kind of crystals can only occur within very narrow limits (98-100 per cent. potassium chlorate) and is deposited from solutions containing less potassium salt than the crystals. The continual separation of solid hence causes the solution to change in composition until that special solution results from which both kinds of crystals are deposited; no further change in composition can occur after this stage is reached.

The complete correspondence with case 4 further indicates that the curve of osmotic pressures is of the form represented in Fig. 6. No data confirming this are, however, at present available. The curve of total concentration (c_1+c_2) of the solution is seen from the table to rise very rapidly between $x=0$ and $x=36.3$. From $x=36.3$ to $x=97.93$, the solution always contains 407 molecules per unit volume. When $x=100$, c_2 is apparently still 407; between $x=98$

and $x=100$, however, the values of $c_1 + c_2$ seem somewhat uncertain, since the numbers change irregularly. The equilibrium between solutions and mixed crystals containing so little thallium chlorate, is perhaps not very readily established. The branch EF of the curve (Fig. 6) deviates but little from the straight line DE ; even for such small differences, however, the curve of total concentration does not show whether the branch EF of the osmotic pressure curve rises or falls.

Since isomorphous substances frequently form both a continuous and a discontinuous series of mixtures, it would at least seem probable that the latter is only possible between *isodimorphous* compounds. The next chapter must here be anticipated and mention made of the fact that chemically simple compounds often assume two, or even three, totally distinct crystalline forms; such substances are termed dimorphous, trimorphous, or generally polymorphous. If two chemically analogous substances each possess two or three crystalline forms, those of the one compound being isomorphous with the analogous forms of the other, such compounds are described as isodimorphous and isotrimorphous respectively.

Several instances are known of isodimorphous substances which conform to case 4 of Roozeboom's classification. Rammelsberg¹ investigated mixtures of ferrous and magnesium sulphates ($\text{FeSO}_4, 7\text{H}_2\text{O}$ and $\text{MgSO}_4, 7\text{H}_2\text{O}$) and also of ferrous and manganous sulphates ($\text{FeSO}_4, 7\text{H}_2\text{O}$ and $\text{MnSO}_4, 7\text{H}_2\text{O}$); after allowing mixed solutions of these salts to crystallize for some time, the residual mother liquors deposited two kinds of mixed crystals which varied but slightly in composition. Retgers² observed similar phenomena with mixtures of sodium and silver chlorates; it is doubtful

¹ Pogg. Ann. xci. 321; Zeits. f. physik. Chem. iii. 542.

² Zeitsch. f. physik. Chem. iii. 452.

whether the behaviour of mixtures of the nitrates of sodium and silver¹, and of the nitrate and chlorate of sodium², is in accordance with case 4 or 5, since the compositions of the solutions were not determined.

It seems highly probable that case 5 is exemplified by mixtures of beryllium sulphate and selenate ($\text{BeSO}_4, 4\text{H}_2\text{O}$ and $\text{BeSeO}_4, 4\text{H}_2\text{O}$); Topsøe's work shows that the two kinds of mixed crystals of limiting composition contain approximately 12 and 20 per cent. of beryllium selenate (BeSeO_4) molecules. The solution from which both kinds of mixed crystals are deposited contains more than 25 per cent. of molecules of the composition BeSeO_4 . Consequently, the relation $y > x$ holds in this case, and the curve plotted between x and y should be of the form shown in Fig. 9. It would also be expected that by continued evaporation of a solution of these two salts, the amount of the tetragonal mixed crystals containing 12 per cent. BeSeO_4 molecules deposited, would decrease, and an increasing proportion of the orthorhombic crystals containing 20 per cent of BeSeO_4 would separate. Mixtures of zinc sulphate ($\text{ZnSO}_4, 7\text{H}_2\text{O}$) with the corresponding sulphates of iron, manganese or copper, and mixtures of magnesium sulphate ($\text{MgSO}_4, 7\text{H}_2\text{O}$) with copper or manganese sulphate apparently behave in accordance with case 5; further study of these pairs of salts is, however, required in order to confirm this.

The behaviour of mixtures of ferric chloride ($\text{Fe}_2\text{Cl}_6, 12\text{H}_2\text{O}$) and ammonium chloride (NH_4Cl) is of quite a special kind and has been investigated by Bakhuis Roozeboom³; these two salts not only form mixed crystals, but also yield a double salt ($4\text{NH}_4\text{Cl}, \text{Fe}_2\text{Cl}_6, 2\text{H}_2\text{O}$). The relation between the solutions and the crystalline

¹ *Zeitsch. f. physik. Chem.* iv. 600.

² *Bull. Soc. Min.* vii. 349.

³ *Zeitsch. f. physik. Chem.* x. 145.

mixtures in equilibrium with them is shown by the following table :—

Number of experiment.	Contents of the Solution				Kind and Composition of the solid crystalline mixture.
	Parts by weight per 100 pts. of Water		Molecules per 100 molecules of Water		
	NH ₄ Cl.	FeCl ₃ .	NH ₄ Cl.	FeCl ₃ .	
1	0	83.88	0	9.30	Fe ₂ Cl ₆ , 12H ₂ O
2	3.24	86.32	1.09	9.57	" " "
3	4.03	91.61	1.36	9.93	" " " + Double Salt
4	5.92	83.64	2.00	9.27	Double Salt
5	8.31	78.77	2.79	8.71	" "
6	9.21	77.54	3.11	8.60	" "
7	12.08	73.20	4.05	8.09	" "
8	15.53	69.01	5.22	7.65	" "
9	19.12	64.83	6.41	7.18	" "
10	22.88	61.28	7.70	6.79	" "
11	32.04	56.00	10.78	6.21	" "
12	23.21	60.83	7.82	6.75	7.29 per cent. of
13	23.05	59.90	7.76	6.64	7.10 Fe ₂ Cl ₆
14	22.63	53.47	7.62	5.94	5.55
15	22.85	49.30	7.69	5.71	5.00
16	22.90	45.42	7.70	5.03	4.40
17	23.00	42.92	7.74	4.76	2.25
18	23.23	39.13	7.81	4.34	3.80
19	23.05	34.56	7.76	3.83	3.06
20	25.33	25.43	8.52	2.82	1.64
21	28.41	15.33	9.60	1.70	0.94
22	32.55	6.15	10.95	0.68	0.31
23	35.30	0	11.88	0	NH ₄ Cl

Crystalline Mixture

An inspection of the table shows that three different solubility curves must be distinguished. The first curve gives the compositions of the saturated solutions containing ferric chloride and ammonium chloride, which can exist in presence of the solid salt, Fe₂Cl₆, 12 H₂O; experiments 1-3 refer to this curve. The second curve (experiments 4-11) gives the solubility of the two salts in presence of the solid double salt (4NH₄Cl, Fe₂Cl₆, 2H₂O) whilst the third curve (experiments 12-22) shows the solubility in presence of mixed crystals of ferric and ammonium chlorides. At the point where the first two curves intersect, the solution is in

equilibrium with both ferric chloride and double salt; similarly, the second and third curves cut at the point at which the solution is in equilibrium with the double salt and the mixed crystals containing the largest amount of iron. These two points are further characterized by being those at which the quantities of the two solid phases present are independent of the composition of the solution, in accordance with Gibbs' rules. At the first point of intersection, addition of solid ferric chloride would not cause the composition of the solution to change; on the other hand, addition of ammonium chloride would only be without influence on the solution until sufficient had been added to change all the solid ferric chloride into double salt. At the other point of intersection of the curves, addition of one or the other simple salt might cause a change in composition of the solution in one or the other direction; so that after equilibrium was again established, the compositions of solution and solid matter would correspond to some point situate only on one or other solubility curve. It is noteworthy that the proportion of iron in the solution and mixed crystals changes abruptly at experiment 17; whether this indicates that the crystalline form of the ferric chloride in the mixed crystals changes into the ordinary cubic form of ammonium chloride or not, cannot yet be decided with certainty. It is, however, significant that at this point the ferric chloride only contains 7-8 molecules of water of crystallization; consequently, the supposition that a cubic modification of ferric chloride ($\text{Fe}_2\text{Cl}_6, 8\text{H}_2\text{O}$) exists, is by no means unjustifiable¹.

Many substances not only furnish isomorphous mixtures having the same crystalline form as their constituents, but also yield another kind of mixtures whose crystalline form has nothing in common with the forms usually assumed

¹ *Zeitsch. f. physik. Chem.* ii. 167.

by the component substances; the author's investigations¹ of thallium and potassium thiosulphates illustrate this. Potassium thiosulphate is ordinarily obtained in anhydrous hexagonal trapezohedral tetartohedral crystals, whilst the corresponding thallium salt crystallizes in the monosymmetric system, although also anhydrous. A mixed solution of the two substances deposits hexagonal or monosymmetric crystals, according as the potassium or the thallium salt preponderates; the former crystals thus simulate the form of the potassium, and the latter that of the thallium, compound. If, however, the solution contains about equal parts of the two substances, a rapid separation of orthorhombic crystals occurs; these have no relation to either the hexagonal or the monosymmetric forms of the pure salts. Their composition only varies within very narrow limits, analyses of two different preparations showing them to contain 84.6 and 84.0 per cent. of $\text{Tl}_2\text{S}_2\text{O}_6$ respectively. The question consequently arises, whether this behaviour is due to the formation of a double salt or of a solid solution; a double salt in which the constituents were in the proportion of one equivalent of potassium to two of thallium contains 82.8 per cent. of $\text{Tl}_2\text{S}_2\text{O}_6$, whilst one containing four equivalents of potassium to nine of thallium would contain 84.3 per cent. of the thallium salt. It is important to note that a solution containing the component salts in the ratio 1K : 2Tl does not at first deposit the orthorhombic crystals; such behaviour points to the conclusion that the latter merely consist of an isomorphous mixture. Such a view is, however, opposed by the observation that sodium thiosulphate, which ordinarily contains two molecules of water of crystallization, also forms a mixture with thallium thiosulphate resembling in composition and crystallographic properties

¹ *Zeitsch. f. Kryst.* vi. 160.

the orthorhombic crystals of the mixed thallium and potassium salts.

The difficulty disappears on a consideration of the following facts. Thallium thiosulphate forms mixed crystals with the corresponding strontium salt, although the latter when pure crystallizes with four molecules of water of crystallization. The crystals, however, are neither hexagonal like those of the strontium salt nor monosymmetric like those of the thallium salt, but are always orthorhombic and have nothing in common with the crystals of the pure individual salts; these orthorhombic crystals are, on the other hand, very closely related in form to the orthorhombic crystals of thallium and potassium thiosulphate, but differ from them in having no constant composition. The obvious conclusion is that both are isomorphous mixtures. From this it might be expected that the strontium salt would also mix with the potassium salt; experiment showed, however, that such mixtures could not be prepared. On the other hand, mixtures which contained the thallium compound in addition to the strontium and potassium salts were readily obtained; these triple mixtures also possessed an orthorhombic form, nearly related to those of the thallium-potassium and thallium-strontium mixtures. It appears further that similar phenomena occur with most thiosulphates; the most remarkable being those observed with mixtures of ammonium thiosulphate and the thiosulphates of the heavy metals.

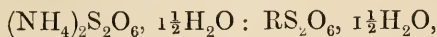
Ammonium thiosulphate, *per se*, crystallizes in the monosymmetric system with $1\frac{1}{2}$ molecules of water, whilst the thiosulphates of the heavy metals crystallize in the anorthic system and contain more water, usually 6 molecules. By allowing mixed solutions to crystallize, however, the salts of the heavy metals cannot be induced to assume the monosymmetric form of ammonium thiosulphate, nor conversely

will the latter take up the anorthic form of the thiosulphates of the heavy metals by mixture with them. Under such circumstances monosymmetric crystals are obtained which do not show the slightest relation to those of the ammonium salt, although belonging to the same system. Up to the present eight mixtures of ammonium thiosulphate with thiosulphates of the heavy metals have been examined; six of these are completely isomorphous, as is shown by the following table. The optic axial plane is in each case perpendicular to the plane of symmetry.

Compound.	Axial Ratios $a : b : c.$	Angle $\beta.$	Optic axial angle for Na light.	Inclination of optic axial plane to vertical axis in obtuse angle $\beta.$
1. Zn-NH ₄ Salt	2.0597 : 1 : 1.2042	89° 8'	71½°	10°
2. Cd-NH ₄ „	2.1299 : 1 : 1.2263	89° 11'	—	—
3. Fe-NH ₄ „	2.0564 : 1 : 1.1907	89° 9'	72°	80°
4. Ni-NH ₄ „	2.0643 : 1 : 1.2077	89° 4'	74½°	83½°
5. Co-NH ₄ „	2.0594 : 1 : 1.2045	89° 6'	74½°	77°
6. Mn-NH ₄ „	2.1289 : 1 : 1.2173	88° 41'	—	—

The composition of these substances is represented by the formula $[(\text{NH}_4)_2\text{R}] \text{S}_2\text{O}_6, 1\frac{1}{2} \text{H}_2\text{O}$, in which $(\text{NH}_4)_2$ and R are isomorphous and consequently replace each other in equivalent proportions; the metal R may be either zinc, cadmium, iron, nickel, cobalt, or manganese. This formula is used in the following table, in order to present more clearly the relationship existing between these substances.

The first five columns give the ratio



as deduced from the analytical results; the numbers in brackets under these are the corresponding values calculated from the nearest assignable molecular ratio of the two salts which is stated in the last column.

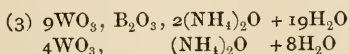
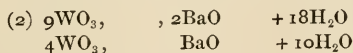
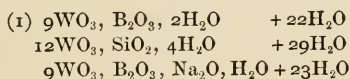
Substance.	$(\text{NH}_4)_2\text{O}$ per cent.	RO.	$(\text{NH}_4)_2\text{S}_2\text{O}_8$, $1\frac{1}{2}\text{H}_2\text{O}$.	RS_2O_6 , $1\frac{1}{2}\text{H}_2\text{O}$.	Sum.	Mole- cular Ratio.
1. Zinc-ammonium salt						
(a) Tabular crystals	18.47 (18.64)	6.39 (6.44)	79.19 (79.93)	19.90 (20.07)	99.09 (100)	2 : 9
(b) Prismatic crystals	18.82 (19.02)	5.82 (5.92)	80.71 (81.57)	18.12 (18.43)	98.83 (100)	1 : 5
2. Cadmium-ammonium salt	14.34 (13.97)	16.40 (17.15)	61.50 (59.89)	38.36 (40.11)	99.86 (100)	1 : 2
3. Iron-ammonium salt						
(a) crystals from solution of $\text{FeO} : (\text{NH}_4)_2\text{O}$	16.81 (17.11)	8.12 (7.88)	72.09 (73.36)	27.43 (26.64)	99.52 (100)	1 : 3
(b) crystals from solution of $\text{FeO} : 4(\text{NH}_4)_2\text{O}$	18.73 (18.77)	5.89 (5.77)	80.32 (80.51)	19.90 (19.49)	100.22 (100)	2 : 9
4. Nickel-ammonium salt	18.64 (18.73)	5.74 (5.97)	79.94 (80.34)	18.90 (19.66)	98.84 (100)	2 : 9
5. Cobalt-ammonium salt	18.69 (18.73)	5.73 (5.97)	80.15 (80.34)	18.86 (19.66)	99.01 (100)	2 : 9
6. Manganese-ammonium salt	18.41 (18.79)	5.63 (5.69)	78.95 (80.58)	19.23 (19.42)	98.18 (100)	2 : 9

The ratio $\text{RS}_2\text{O}_6, 1\frac{1}{2}\text{H}_2\text{O} : (\text{NH}_4)_2\text{S}_2\text{O}_8, 1\frac{1}{2}\text{H}_2\text{O}$ varies from 1 : 5 in the zinc salt to 1 : 2 in the cobalt salt; in most cases, however, it approximates to 2 : 9. This variation in the proportion of combination is opposed to the recognition of such compounds as true double salts, that is, as molecular compounds in constant proportion; the iron salt, for instance, undoubtedly forms two such mixtures. The recent researches of Roozeboom render it far more probable that these salts are deposited when the osmotic pressure of the solution has either a maximum or a minimum value. A definite conclusion as to these phenomena can only be obtained from an investigation of both solution and crystals; the prosecution of such an inquiry would, however, be attended with considerable difficulty, owing to the instability of the compounds concerned.

Special mention is necessary of the power of forming mixed crystals, possessed by certain substances which,

although endowed with similar crystalline forms, are dissimilar in respect to their chemical properties. According to the observations of Marignac, niobium-tungsten fluotitanate and oxyfluotitanate are isomorphous; so also are the fluosilicate, fluotitanate, fluostannate, oxyfluoniobate and oxyfluomolybdate of zinc. Further, the acid silicotungstates of barium and calcium and the free silicotungstic acid are isomorphous.

Scheibler has also shown that several metatungstates which contain different proportions of water of crystallization, possess quite similar forms. The most remarkable case is, however, that of the isomorphism of certain silicotungstates and borotungstates. According to Klein's investigations¹, the compounds indicated in the following table not only possess similar crystalline forms, but also yield mixed crystals:—



In order to explain facts of this kind, the above-named observers were forced to extend and specially modify the law of isomorphism, inasmuch as the older views and observations were insufficient to account for the formation of isomorphous mixtures of such substances, although double compounds might well be produced.

During recent years, a considerable number of examples have been recorded of substances which form isomorphous

¹ *Compt. rend.* xcv. 781; compare also *Zeitsch. f. Kryst.* ix. 409.

mixtures, but are at the same time very slightly, or not at all, related in a chemical sense. The explanation of such cases will probably only be found after more extended examination by the method employed by Bakhuis Roozeboom.

Note.—In addition to the example quoted on p. 121, see also, for other cases, Muthmann and Kuntze, *Zeitsch f. Kryst.* xxiii. 368.

CHAPTER XIX.

THE PROPERTIES OF MIXED CRYSTALS.

MANY comparative studies of the properties of mixed crystals have been made during the search for some elucidation of the nature of crystallization, and of the kind of combination existing in isomorphous mixtures. The prosecution of such investigations is, however, attended with great difficulty, since homogeneous products can only be obtained by the expenditure of considerable time and trouble. The fact that really homogeneous crystalline mixtures can exist, is vouched for by their frequent occurrence amongst minerals such as olivine, alstonite, barytocelestine, &c.

The lack of homogeneity in mixed crystals depends essentially upon a kind of stratified structure, the crystalline individuals being built up of layers of different chemical composition. According to the previous argument respecting crystalline growth, such a phenomenon must necessarily occur, if the prevailing conditions undergo any change during the process of crystallization; such changes may be caused by an alteration in the composition of the solution, owing either to the gradual deposition of solid matter, or to a quick separation due to cooling or rapid evaporation. The difference in the successive layers deposited in unit time will naturally be the greater as these changes are the more strongly marked; further,

a crystal of one substance will grow if placed in the saturated solution of another and an isomorphous substance, because layers of the dissolved substance become deposited upon the growing crystal.

These non-homogeneous mixed crystals possess considerable scientific interest, inasmuch as they furnish a certain proof that different kinds of structural units have the power of uniting to form a single individual crystal. On attempting, however, to generalize this principle, without in some way modifying it, and thence concluding that homogeneous mixed crystals could be built up from structural units of different kinds, results are attained which are no longer in accordance with the facts.

So far as the geometrical properties are concerned, it was early supposed that the angles of mixed crystals should, without exception, lie between those of their components; this is the case in most of the rhombohedral carbonates and of the plagioclases. Groth¹, however, showed that certain well-characterized mixed crystals of potassium perchlorate and potassium permanganate gave angular measurements which lay outside the limits imposed by the angles of the individual salts. Arzruni² and Neminar³ found similar exceptions with celestine and barytocelestine, whilst Sansoni⁴ also observed such phenomena amongst some double salts of the aliphatic acids.

The optical properties of mixed crystals are of greater interest than the geometrical ones, affording, as they do, the best means of certifying the homogeneity of an individual crystal. According to Dufet's observations⁵ the refractive indices of isomorphous mixtures vary directly with the chemical composition. Dufet started with the assumption

¹ *Pogg. Ann.* cxxxiii. 193.

² *Zeitsch. d. d. geol. Ges.* xxiv. 484.

³ *Tschermaks Min. Mitt.* 1876, 59.

⁴ *Zeitsch. f. Kryst.* vi. 67.

⁵ *Compt. rend.* lxxxvi. 881.

that the time occupied by a ray of light in traversing a certain thickness of a mixed crystal, is equal to the sum of the times in which the ray is propagated through the layers of the individual constituents which it traverses. The refractive index N of the mixture may then be calculated from the formula

$$N = \frac{pn + p_1n_1}{p + p_1},$$

where n and n_1 are the refractive indices of the components, and p and p_1 their quantities expressed in equivalents.

Another theory of light propagation in isomorphous mixtures has been mathematically developed by Mallard¹. He bases the investigation on the general supposition that the component substances preserve their special crystallographic and optical properties unaltered in the mixtures, or more particularly that the elastic forces developed in a mixed crystal by light vibrations, should be the resultants of the elastic forces operative in each of the component substances. Thus let A , B , and C represent in magnitude the optical elasticities along the three axes of an orthorhombic mixed crystal, and a , b , and c , and α , β , and γ the corresponding values for the two components; then the relation which subsists is expressed by the equations

$$A^2 = ua^2 + v\alpha^2$$

$$B^2 = ub^2 + v\beta^2$$

$$C^2 = uc^2 + v\gamma^2$$

where u and v represent the percentage numbers of molecules of the two constituents respectively present in the mixed crystal.

Both Mallard and Dufet's laws agree that the optical properties of two isomorphous substances are not appreciably

¹ *Zeitsch. f. Kryst.* vi. 612.

affected by combination of the substances to form a mixed crystal. It is practically of little moment whether the refractive index of the mixture is calculated from one or the other formula in any special case; great experimental difficulties consequently attend any attempt to assign greater correctness or greater probability to either law. The observations which have been made agree with both laws, either equally well or equally badly; in general, however, the above laws seem to be confirmed, and therefore their discoverers conclude that isomorphous mixtures are the result of a purely physical process, such as would be obtained by arranging structural units of different kinds side by side.

A full confirmation of the validity of laws of this kind is much to be desired, as they would afford a means of deciding whether isomorphous mixtures or definite chemical compounds are being dealt with in certain cases. It must, however, be remarked that from the present condition of optics, and more especially from our knowledge of the refractive properties of chemical substances, no appreciable deviation from these laws would be expected, even if isomorphous mixtures really are chemical compounds. The refraction equivalents of elements or groups of atoms undergo no appreciable change, so long as the bonds between the atoms are of similar kinds, or the individuality of the groups remains essentially unchanged. Further, the chemical bonds uniting isomorphous substances are certainly so feeble, that in any case their influence on the refractive power would probably be but small even when compared with the discrepancies noticed between chemical compounds of the same type. The correspondence of most of the observations with the above-mentioned laws cannot therefore be considered as constituting a proof, even if contradictory observations be rejected on the ground of non-homogeneity

of the crystals. The measurement of the refractive indices of artificial crystals, and more particularly of mixed crystals, is attended with so much difficulty, and the values obtained with the better characterized isomorphous mixtures differ so slightly from the calculated numbers, that a definite solution of the problem by experimental methods is hardly to be expected.

Wyrouboff correctly recognized that a better criterion of the truth of these laws is to be found in measurements of the optic axial angle; a small deviation from the law in the case of the median refractive index has a very considerable effect on the magnitude of the axial angle, especially when the double refraction is weak. Several examples of such cases may be here quoted.

The following table was arranged by Mallard¹ from measurements made by Wyrouboff on mixtures of potassium sulphate and chromate:—

Molecules of K_2CrO_4 in percentages.	Half the optic axial angle measured in oil for red light.		
	Observed.	Calculated.	Difference = Δ .
0	$57^\circ 53'$	—	—
4.93	$57^\circ 0'$	$49^\circ 48'$	$+ 7^\circ 12'$
6.53	$50^\circ 12'$	$47^\circ 48'$	$+ 2^\circ 24'$
10.04	$44^\circ —$	$42^\circ 12'$	$+ 1^\circ 38'$
23.25	$36^\circ 45'$	$37^\circ 30'$	$- 0^\circ 45'$
40.55	$31^\circ 40'$	$33^\circ 20'$	$- 1^\circ 40'$
100.00	$29^\circ 45'$	—	—

The calculated semi-axial angles may be considered as liable to an error of 2° , owing to inexact measurements of the refractive powers of the constituent salts; an error of $30'$ is also possible in the direct measurements of the half-axial angles. A total difference of $2\frac{1}{2}^\circ$ between the observed and calculated values is hence quite possible. So

¹ *Bull. de la Soc. Min. de France*, iii. 3.

large a difference as 7° , however, seems to lie outside the limits of experimental error, and scarcely agrees with the laws stated above. Since, however, other measurements made by Wyruboff agree satisfactorily with the calculated values it may be considered as demonstrated that the formulæ express the facts. Such a proof can indeed lay no claim to unconditional recognition, especially when it is considered that great deviations from the law are scarcely to be expected, and that consequently any individual anomalous case would be of extraordinary importance.

Wyruboff¹ has investigated one case which is in obvious contradiction to the laws of Mallard and Dufet. The tartrates of ammonium and thallium are completely isomorphous, both belong to the monosymmetric system, show nearly identical angles, and crystallize together in all proportions. The ammonium salt has a cleavage parallel to the basal plane, the optic axes lie in the plane of symmetry, and the optic axial angle is $42^\circ 38'$. The thallium salt, on the other hand, shows no cleavage, the optic axial plane is perpendicular to the plane of symmetry, and the axial angle is $59\frac{1}{2}^\circ$. The isomorphous mixtures of the two salts, however, invariably show the same cleavage and optic axial plane as the ammonium salt; a mixture containing 88.7 per cent. of the thallium salt was moreover obtained, in which the optic axial angle was found to be $43^\circ 30'$, being thus completely identical with that of the pure ammonium salt.

During recent years Retgers² has entered upon a study of the specific gravities and molecular volumes of isomorphous mixtures. The results show that the molecular volumes of such mixtures simply possess additive values, and may thus be directly calculated from the chemical com-

¹ *Zeitsch. f. Kryst.* xiii. 648.

² *Zeitsch. f. physik. Chem.* from vol. iii.

position; the specific gravity is therefore directly proportional to the composition, so long as the crystalline form persists unaltered. The molecular volumes of chemical compounds are however, in general, the sums of the corresponding atomic volumes, so long as no special difference in the chemical bonds or linkages comes into play; further, determinations of the density of artificial crystals are usually attended by considerable errors. Any other result of such an investigation than that stated above is consequently scarcely conceivable, and the study of the optical properties yields results of much greater importance to the subject of isomorphism.

The validity of Dufet's law has but little bearing on the question as to whether van't Hoff's application of the term 'solid solutions' to isomorphous mixtures be correct or not, inasmuch as the term solid solution simply carries with it the idea that the physical properties alter continuously with the chemical composition. This, according to the above-mentioned investigations, seems to be perfectly true. No more explicit signification than this can be given to the term 'solid solution,' since even liquid solutions frequently occur, in which the physical properties cannot be calculated additively from those of their constituents.

CHAPTER XX.

GENERAL CONCLUSIONS RESPECTING ISOMORPHISM.

FROM the above discussion of the available observations relating to isomorphism, it is evident that the properties of mixed crystals are such as might be expected from van't Hoff's view that crystalline mixtures should be regarded as solid solutions. The correctness of this view is certainly not demonstrated; but no hypothesis ever is, in the end, absolutely proven, its scientific value being principally determined by the completeness with which it unites the facts, and the stimulus which it gives to investigation. In this last respect the new theory is quite unique.

The extent to which solid substances can mix to form a homogeneous solid solution is greatly limited, and such solutions are of comparatively rare occurrence; they are to be met with only amongst metallic alloys and isomorphous mixtures. Amongst gases this power of mixing to give a homogeneous product is a general one, and occurs to an unlimited extent. The property is already greatly limited in the case of liquids; some liquids are completely immiscible, some only mix within certain limits, whilst others are miscible in all proportions. Relations of the same kind as for solid substances thus hold here, only the power of forming mixtures is of less frequent occurrence, and is much more restricted, in the case of solids.

No explanation of this peculiar behaviour of liquids and solids has yet been given. In the case of the latter, mixture usually occurs only amongst substances of chemically analogous constitution, which, moreover, possess similar crystalline forms, being hence isomorphous. In recent years, however, there has been a considerable increase in the number of substances known which, whilst they do not satisfy these conditions, yet form homogeneous solid solutions. Consequently, the property of mixed crystallization cannot be considered as a criterion of isomorphism, but, on the other hand, the possession of similar crystalline forms is of the utmost importance as indicating that two substances will form isomorphous mixtures. Of course a perfect appreciation of the conditions governing isomorphism will only be attained when a complete theory of the state of aggregation of solid bodies has been built up on an experimental basis:—a theory such as the present one of the gaseous condition. The hypothesis of solid solutions, however, may well lead the way to this.

A homogeneous mixture of two solid substances, of which one is present in only a small proportion, is thus a 'dilute' solid solution; the two constituents can also be distinguished as the solvent and the dissolved substance. The question now arises, whether the dissolved substance exercises a definite partial pressure (osmotic pressure) analogous to that exerted in liquid solutions. The employment of semipermeable membranes, such as were used in the latter case, is obviously impossible in the case of a solid system; the power of diffusion possessed by substances contained in solid solution, however, unmistakably demonstrates the operation of an expansive force, which may be compared to the osmotic pressure. Several instances of this power of diffusion of solid bodies may be here recalled to mind. Hydrogen readily dissolves in platinum or

palladium, and then gradually permeates the whole mass of the metal; carbon is absorbed by hot porcelain crucibles and ultimately passes through them; according to Spring, solid barium sulphate and sodium carbonate act upon each other until a condition of equilibrium is attained; such behaviour seems scarcely possible unless mutual molecular penetration occurs. Lastly, the fact that many solid bodies are electrolytes, indicates the possibility of diffusion in the solid state, since according to modern views the ionic carriage of electricity is hardly separable from diffusion.

Further, if the possibility of diffusion, and consequently of the exertion of partial pressures, be admitted in solid solutions, it can be shown that these partial pressures determining the diffusion of dissolved substances from concentrated parts of the solution to the more dilute, are subject to the same laws as the osmotic pressures, i. e. to the laws of gases. The laws which govern ordinary liquid solutions should thus be equally applicable to solid solutions, and amongst others, those laws which underlie the methods of determining molecular weights. As Nernst has very suggestively pointed out¹, a clue is thus obtained to an exact method for estimating the comparative size of crystalline molecules. From the observations of Roozeboom on crystalline mixtures of thallium and potassium chlorates Nernst arrives at the view that potassium chlorate in the solid solution has a molecular weight corresponding to KClO_3 ; this he deduces by applying his so-called 'law of distribution,' according to which the coefficient of distribution of a substance between two solvents in contact with each other is a constant at a given temperature, if the molecular weight in the two solvents be the same.

¹ *Zeitsch. f. physik. Chem.* ix. 137.

CHAPTER XXI.

HISTORICAL SKETCH OF PHYSICAL ISOMERISM.

ACCORDING to Haüy's views, which are described above, it was just as little possible that one and the same substance should possess two crystalline forms, as that two different substances should exhibit the same form. The vigour with which Haüy combated everything favouring the former possibility will be readily understood from what has been previously said.

The earliest observations of any importance in this respect were made towards the end of the last century. The chemical identity of rutile and anatase was then recognized by Vauquelin ; these two minerals, although quite different in crystalline form, yet belong to the same system. De l'Isle had clearly distinguished between calcite and aragonite some time before, supporting his conclusions principally upon crystallographic evidence ; the distinction had, however, become very doubtful owing to the establishment of the chemical identity of the two minerals by Klaproth in 1788. A critical re-investigation of the two minerals was consequently instituted by Brochant and Haüy and resulted in the confirmation of the difference in crystalline form ; doubts were then raised as to the accuracy of Klaproth's analyses ; these, however, were completely set at rest by Thénard, who in 1800 repeated the chemical examination, employing every means at that time available for ensuring

accuracy. Nevertheless, Haüy refused to trust the results, and in the following year expressed the opinion that more extended investigation would reveal chemical differences between calcite and aragonite. Such differences indeed actually seemed to exist, for Stromeyer, after discovering strontium in 1813, made the observation that all the aragonite examined by him contained a greater or less proportion of strontium, whilst calcite, on the other hand, was free from this element. Haüy was thus enabled to explain the fact that aragonite is an orthorhombic mineral, whilst calcite belongs to the rhombohedral system; he supposed that strontium carbonate possesses a great power of crystallization, and thus, when present in small quantities in calcium carbonate, constrains the latter to assume the orthorhombic form. Haüy's views thus seemed to receive a brilliant confirmation, and mineralogists were quite prepared to consider all future cases of a similar kind as dependent on an incomplete knowledge of the chemical composition of the substances concerned.

As has been already shown¹, Haüy's hypothesis was to a great extent modified in 1819 by Mitscherlich's discovery; to Mitscherlich also was due the incontrovertible proof that one and the same substance can actually exist in two different crystalline modifications. During his work on the phosphates and arsenates in 1821 he observed that sodium dihydrogen phosphate $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ was an exception to the general rule, in that its crystalline form differed from that of the corresponding arsenate, although the same amount of water of crystallization was present in both salts. He was therefore led to vary the conditions of crystallization, and on one occasion obtained the phosphate in the same form as the arsenate. Although on the whole the fact seemed to him doubtful and he did not publish it, yet, as has been

¹ Chap. XVI.

mentioned above, it was not altogether without influence on his definition of isomorphism, which dates from the same year. In 1823 Mitscherlich made the further observation that sulphur behaves in much the same way as sodium phosphate; by slowly cooling liquid sulphur, monosymmetric prisms are obtained, whilst the natural crystals and those deposited from solution are orthorhombic pyramids. This, then, was a clear proof that one and the same chemical substance, and even a chemical element, may possess two crystalline forms. Haüy, however, did not live to witness this last correction of his views; he died in 1821.

The name *dimorphism* was reserved for this newly-discovered phenomenon, and substances by which it is exhibited, such as sulphur, sodium phosphate, and calcium carbonate, were described as *dimorphous*.

Numerous examples of dimorphism were soon noticed; in 1827 it was observed that the sulphates and selenates of magnesium, zinc, and nickel crystallize both in the tetragonal and orthorhombic systems with the same proportion of water of crystallization. The deposition of one or the other form is conditioned by the temperature, tetragonal crystals separating from warm solutions, whilst the orthorhombic forms are deposited in the cold. In the following year it was discovered that single substances could assume not only two but three, and sometimes more, different crystalline forms; such substances are consequently described as *trimorphous* and *polymorphous* respectively.

This discovery seems to have had a certain influence upon pure chemistry. Until this time the principles underlying this science had much in common with Haüy's views; the various physical and chemical states of solid bodies were supposed to be accompanied by differences in percentage composition, and any facts not agreeing with

this supposition were attributed to errors of observation. In 1824 Liebig showed that fulminuric acid had the percentage composition which Wöhler in the previous year had assigned to cyanic acid. If the analogous observations of Mitscherlich on polymorphism had been unknown, this fact would certainly have been received with grave suspicion; other cases of the same kind, recorded a little later by Faraday and by Clark, would also have fared similarly instead of meeting with speedy recognition. Berzelius, who was recognized as the greatest authority in chemical science, immediately took these discoveries under his protection and made most important contributions to their development. Thus, in 1828, he distinguished between the different crystalline forms of tin oxide, and two years later established the identity in composition of racemic and tartaric acids. He termed such substances as these, *isomerides*, and described the phenomenon itself as *isomerism*.

The cause of isomerism was at this time just as doubtful as was that of dimorphism, and many attempts were made to trace the two phenomena to the same source. In course of time, however, a sharp distinction was made between *chemical isomerism*, and dimorphism or *physical isomerism*. A consideration of chemical isomerism is not within the scope of the present work, and the mutual relations of the two subjects will therefore not be more fully discussed.

CHAPTER XXII.

THE PROPERTIES OF PHYSICAL ISOMERIDES.

DIFFERENCES between two substances possessing the same percentage composition may be merely of a physical nature—affecting only the state of aggregation, crystalline form, colour, hardness, density, and melting point, and causing no essential alteration in a chemical sense—or may also extend to chemical properties. In the latter case the differences are due to the different ways in which the atoms are grouped together in the chemical molecule; this has been conclusively demonstrated by numberless investigations of ‘chemical isomerides.’ Substances which differ physically, but not chemically, and belong to the first category with which alone we are at present concerned, have only received careful consideration during recent years. The cause of the differences seems to lie merely in the various ways in which the chemical molecules are grouped together to form more complex molecules which have been variously named physical molecules, liquid molecules, or structural units. Such substances have been described by Lehmann¹ as ‘physical isomerides’; at first this term was usually only applied to organic compounds, whilst isomerism of the same kind, when occurring in the province of inorganic chemistry, was described as allotropy, heteromorphism, dimorphism, polymorphism or polysymmetry.

¹ *Zeitsch. f. Kryst.* i. 97.

It is often by no means easy to decide whether a certain case is an example of physical or of chemical isomerism ; with certain elements, such as phosphorus and carbon, distinction may be possible. Such far-reaching differences as exist between graphite and diamond, or yellow and red phosphorus, can hardly be ascribed to mere differences in the number of chemical molecules which combine to form one physical molecule. It is extremely significant that the difference between ordinary oxygen and ozone can be with certainty assigned to the fact that the chemical molecules contain two and three atoms respectively. Reasoning from analogy, it seems justifiable to conclude that the cases of carbon and phosphorus, and of so-called allotropic modifications generally, are instances of what is termed *chemical polymerism*.

Special mention should be made of a number of substances, whose modifications, though scarcely distinguishable by purely chemical means, are more readily distinguished than those of other isomerides in a particular way. These substances form the class of 'optically active' compounds, i. e. those which, when in the liquid state, rotate the plane of polarization of light.

Two modifications of tartaric acid are known, which, when dissolved in a convenient solvent, rotate the plane of polarization of light to an equal extent, but in opposite directions ; the one is thus dextro-rotatory and the other lævo-rotatory. These substances crystallize without water of crystallization and are absolutely similar in chemical properties ; further, as would be expected, they both crystallize in the same system (the monosymmetric) and have exactly the same crystallographic dimensions. The crystals are, however, hemimorphic, and the two modifications show the remarkable crystallographic difference, that the one always presents associated with the clinodome, though

not necessarily in a conspicuous manner, the right semi-form, whilst the other always exhibits the left semi-form.

According to the work of Le Bel and van't Hoff, the optical difference between the dextro- and lævo-tartaric acids is due to the different arrangement in space of the atoms composing the chemical molecules; such cases are therefore instances of chemical isomerism. The cause of the slight crystallographic differences observed between such '*optical isomerides*' is thus to be found in the different configurations of the molecules of the optically active modifications of a substance. The general rule is found to hold that optical isomerides crystallize in hemihedral or hemimorphic forms which are at the same time enantiomorphous; that is to say, the crystals of the two modifications are related to each other as a right-hand glove is related to a left-hand one, or as the figure of a man is related to its image in a mirror. Right-handed forms are thus present on crystals of the one modification, and left-handed forms upon those of the other isomeride. This rule only holds for such optical isomerides as rotate the plane of polarization to the same extent, but in opposite directions, and which may hence be termed '*optical antipodes*'; the converse of the rule, however, is not true, since many substances are known which, though crystallizing in hemihedral or hemimorphic forms, are not optically active in solution.

Racemic acid (para-tartaric acid) possesses the same composition and the same chemical properties as dextro- and lævo-tartaric acids, but differs from them in having no effect on the plane of polarization of light; it is thus optically inactive in solution. It is prepared by crystallizing a mixture of equal weights of the two optically active modifications; whilst, however, the active acids crystallize without water, racemic acid separates from

solution with water of crystallization, consequently no crystallographic comparison is possible. Further, the salts of tartaric and racemic acids, respectively, always contain different proportions of water of crystallization, so that their crystalline forms are not comparable. Unfortunately, but few cases are known in which the racemic form of a substance crystallizes with the same proportion of solvent as its optically active components. One such case, however, has been described by Armstrong and Pope¹. Three modifications of sobrerol may be obtained, i. e. lævo-, dextro-, and para-sobrerols. The two active modifications have identical chemical properties and crystallize in hemimorphic, monosymmetric prisms; the crystals of these optical antipodes are consequently enantiomorphous. On crystallizing a mixture of equal weights of each, holohedral orthorhombic crystals of the racemic modification are obtained. A very intimate crystallographic relationship exists between the crystalline forms of the active and inactive substances, as will be seen from the axial ratios given below :—

$$\begin{array}{lcl}
 \text{Active Sobrerol} & \} & \{ a : b : c = 2.4113 : 1 : 0.8531 \\
 \text{(Monosymmetric)} & \} & \{ \beta = 83^{\circ} 38'. \\
 \text{Inactive Sobrerol} & \} & \{ a : b : c = 2.4242 : 1 : 0.8268 \\
 \text{(Orthorhombic)} & \} & \{ (\beta = 90^{\circ}).
 \end{array}$$

It is noteworthy, that Pasteur found one salt of racemic acid which could be split up by crystallization; if a crystal of sodium ammonium dextro- or lævo-tartrate be brought into a solution of sodium ammonium racemate saturated at 28°, the salt of the dextro- or lævo-acid respectively separates. This property of combining together to form an inactive racemic modification is apparently not possessed by all pairs of optical antipodes; several instances have

¹ *Journ. Chem. Soc.* 1891, 315.

been described in which no definite racemic modification could be prepared. The two oppositely active modifications when crystallized together seem sometimes to form partially interpenetrant twins, as in the case of the active camphorsulphonic chlorides described by Kipping and Pope¹. Similar instances have been described by Menozzi and Appiani².

Numbers of substances behave similarly to the tartaric acids, and crystallization has frequently proved a valuable aid in the separation of the two active modifications of a compound. These facts are of the greatest crystallographic importance, more particularly in connexion with the theory of crystalline structure, inasmuch as they furnish a proof that slight changes in the chemical molecule find expression in the external crystalline form³; although this alteration is but one of the many causes influencing crystalline structure.

Optically active and so-called allotropic substances are thus chemical isomerides and polymerides respectively, and owe their existence to differences in the constitution of the chemical molecule; all the cases of so-called physical isomerism are, on the other hand, to be ascribed to the different numbers and groupings of similar chemical molecules to form one physical molecule. In considering the properties of the physically isomeric modifications of a substance, it has first to be noted that these modifications are in general characterized by the possession of quite dissimilar crystalline forms; such substances are therefore ordinarily described as heteromorphous, dimorphous, trimorphous, or, in a more general sense, as polymorphous. By a careful consideration of their various crystalline forms,

¹ *Journ. Chem. Soc.* 1893, 554.

² *Gaz. chim. ital.* 1894, xxiv. i. 370.

³ Sohncke assigns the immediate cause of hemimorphism to the particular structure of the chemical molecules.

Pasteur first showed, that, though belonging to different crystalline systems, they often present similar angles; further, those modifications which belong to crystalline systems of lower symmetry are frequently seen, from the magnitudes of their angles, to approach the symmetry possessed by the more symmetrical modifications. The optical properties, at the same time, exhibit remarkable analogies.

Thus, calcium carbonate crystallizes in the rhombohedral system as calcite, and in the orthorhombic as aragonite. The prism angle of the latter is $116^{\circ} 13'$, and when the prism is accompanied by the brachypinacoid, the combination has much the same appearance as a hexagonal prism of calcite, of which the angle is 120° . This approximation to, or mimicry of, the higher hexagonal symmetry is frequently increased by complicated twinning upon the primary prism. Similar relations hold between the two modifications of arsenic trioxide and of antimony trioxide. The former occurs in nature both as the cubic mineral arsenolite and as the orthorhombic one claudetite; antimony trioxide is found in similar forms as senarmonite and valentinite. Between the orthorhombic and cubic forms the remarkable relation exists, that the orthorhombic prism angle ($70^{\circ} 32'$) has the same value as the cubic octahedron angle. Further, the orthorhombic and cubic minerals are respectively isomorphous. Substances of such analogous chemical constitution, which exhibit at the same time isomorphism and dimorphism, are termed '*isodimorphous*'; if trimorphism is concerned, the substances are said to be '*isotrimorphous*.' Examples of isodimorphism and even of isotrimorphism are not uncommon; the two physically isomeric groups of the pyroxenes and amphiboles may be quoted as an instance. Each of these two groups is composed of minerals which belong to three different

crystalline systems, i. e. the orthorhombic, monosymmetric, and anorthic, and all possess analogous compositions; the members of each group, even when belonging to different systems, possess the closest possible resemblance to each other, in respect to their angles, cleavages, and optical properties. Further, the corresponding members of each group show a great similarity in form and optical properties; the sharp distinction between them only becomes evident when the cleavage is considered. Two kinds of physical isomerism must here be carefully distinguished: the one existing between the different members of one and the same group, which, in spite of the various crystalline systems to which the members belong, only introduces slight differences; and the other kind of isomerism which finds expression in the corresponding members of the two groups. Both kinds certainly arise from different causes¹.

The various feldspars are related to each other in much the same way as the amphiboles and pyroxenes. It is frequently observed that one physically isomeric modification of a substance is characterized by a tendency to affect a certain habit in its growth, and then by repeated twinning to mimic the higher symmetry of other modifications of the same substance. Scacchi recognizes in this a special property of physical isomerides to which he gives the name 'polysymmetry.'

So far as purely physical properties are concerned, the usual character by which the modifications of a substance are distinguished is the fusibility. Each modification, however, does not necessarily possess a particular melting point; one modification is stable at the high temperature, and the other isomerides are often converted by heat into this form before liquefaction can take

¹ Compare p. 166.

place. The following table gives some examples of the melting points of physically isomeric substances:—

Name.	Formula.	System.	Melting Point.
Hydroquinone	$C_6H_4(OH)_2$	1. Monosymmetric 2. Hexagonal	169° 167°
Benzophenone	$(C_6H_5)_2CO$	1. Orthorhombic 2. Monosymmetric	49° 26°
Metachloronitrobenzene	$C_6H_4ClNO_2$	1. Orthorhombic (?) 2. Unknown	44° 23°
Nitrometachloronitrobenzene	$C_6H_3Cl(NO_2)_2$	1. Monosymmetric 2. Monosymmetric 3. Orthorhombic	36° 37° 39°
Nitrotetrabromobenzene	$C_6HBr_4NO_2$	1. Unknown 2. Unknown	96° 60°
Paratolylphenylketone	$C_6H_5 \cdot CO \cdot C_7H_7$	1. Monosymmetric 2. Hexagonal	58° 55°
Ethylidene dibenzhydroxamate	$(C_6H_5)_2CO > NO$ C_2H_5	1. Orthorhombic 2. Anorthic	58° 63°
Benzaniline benzhydroxylamine	$C_7H_5O \searrow N$ $C_6H_7O_2 \searrow$ $C_7H_5O_2 \searrow$	1. Orthorhombic 2. Monosymmetric 3. Anorthic	124° 110° 113°
Dibromopropionic acid	$CH_3 \cdot CBr_2 \cdot COOH$	1. Orthorhombic (?) 2. Tetragonal	64° 51°

From the melting points given above, it will be observed that since physical isomerism is by no means a rare phenomenon amongst organic substances, melting-point determinations lose somewhat in importance as a means of characterizing and identifying compounds. The other physical properties of physical isomerides have hitherto been but seldom subjected to thorough comparative study; so far as is known, however, the specific gravity, hardness, and also the solubility of such isomerides are, as a rule,

different, very considerable differences in these respects having been observed. Much more attention has been paid to the conditions under which the various modifications of a substance are formed, and under which they are convertible one into the other. It has thus been established that an alteration in the potential energy of the material always accompanies the conversion of one modification into another; this change may cause, firstly, a development of heat, or, secondly, an absorption of heat. Changes of the first kind are naturally the most readily followed, and have hitherto been exclusively studied. From this redistribution of heat it is at once evident that temperature plays the most important part in the mutual interconversion of physical isomerides; it is also found, however, that contamination with foreign substances is not without influence in some cases on the formation of one or another modification.

Thus Gustav Rose¹ observed that the amorphous precipitate formed by adding ammonium carbonate to cold calcium chloride solution after a time becomes crystalline and acquires the crystalline form and specific gravity (2.72) of calcite. On precipitating hot solutions or heating a solution of calcium carbonate in carbonic acid, a crystalline deposit is obtained which has the form and specific gravity (2.95) of aragonite. This changes to calcite on remaining in contact with water in the cold; if, however, the precipitate has been previously separated and dried, the change into calcite cannot be caused to occur. It therefore seems justifiable to conclude that the temperature alone is concerned in the formation of one or the other modification of calcium carbonate. Further investigation shows, however, that a low temperature is by no means essential to the formation of calcite; the latter can be obtained at 100°,

¹ *Pogg. Ann.* cxi. 156; cxii. 43.

and conversely aragonite can be prepared at ordinary temperatures. Credner¹ showed that, on standing, a solution of calcium carbonate in carbonic acid contaminated with an alkaline silicate, deposits calcite crystals showing very brilliant faces and a large number of forms. If, however, strontium or lead carbonate be the impurity in the solution, only aragonite crystals are deposited; these are obtained with the greater ease and certainty as the quantity of foreign carbonate added is the larger. Consequently, an aqueous solution of pure calcium carbonate, under ordinary conditions deposits either calcite or aragonite with equal facility; as the temperature is raised, however, the conditions become more favourable to the formation of the latter modification, although no sharp line of demarcation can be drawn². Further, when an aragonite crystal is subjected to a low red heat it crumbles to a crystalline powder, which is conclusively proved to consist of calcite by specific gravity determinations.

The phenomena exhibited by the various modifications of sulphur are of especial interest. Mitscherlich first found that the temperature at which sulphur assumes the solid form determines the particular isomeric form assumed by the element. Sulphur crystallizes in the monosymmetric system on solidifying from the molten state; when crystallized from solution at the ordinary temperature, orthorhombic crystals are obtained. It has more recently been shown, however, that the orthorhombic modification of sulphur may be prepared by crystallizing sulphur from its solutions at high temperatures. The monosymmetric crystals, obtained by cooling molten sulphur, gradually and spontaneously change into the orthorhombic form on standing at ordinary temperatures; further, the reverse

¹ *Journ. f. prakt. Chem.* 1870, (2) ii. 292.

² Compare Vater, *Zeitsch. f. Kryst.* 1893, xxi. 433; 1894, xxii. 209.

change is also brought about by heating the orthorhombic form just below its melting point. There is, however, a definite temperature at which the two modifications are formed with equal readiness; at this temperature the one modification does not change into the other, i. e. the one modification is not formed at the cost of the other.

Gernez¹ has thoroughly followed the course of formation and interconversion of these two isomerides. If an orthorhombic sulphur crystal be left in contact with a mass of the monosymmetric variety at the ordinary temperature, conversion of the whole mass into the orthorhombic form commences. The conversion proceeds from the original point of contact with the greatest regularity, and causes the previously transparent mass to become opaque; the speed at which the change proceeds is greater or less, as the temperature is higher or lower. Near the neutral temperature—which is equally favourable to the formation of either modification—the change is very slow. Thus, with one preparation obtained by melting the element at 129.5° and solidifying it at 88.9° , it was subsequently observed that at 95.1° , conversion only proceeded a distance of 10 m.m. in the mass during twenty-four hours, whilst at 94.6° the same amount of change occurred in nine and a half hours. The speed increased considerably as the temperature fell, until at 50° the maximum velocity of conversion was reached; below this temperature the speed decreased until at 23° the conversion proceeded at the same rate as at 94.6° . The speed of conversion is greater, other conditions remaining the same, when the monosymmetric modification is obtained by allowing the molten sulphur to crystallize in contact with a crystal of the monosymmetric form.

Certain other conditions also exert an influence on the

¹ *Ann. de Chim. et de Phys.* (6) vii. 233; compare *Zeitsch. f. Kryst.* xiii. 427.

rapidity of conversion, as, for instance, the temperature to which the sulphur has been heated during the fusion. Monosymmetric sulphur deposited from a magma fused at a low temperature, changes into the other variety with a constant velocity; the speed of change is, however, greater for sulphur which has been more strongly heated. These differences between the velocities of conversion become less distinct as the interval of time between the crystallization and the commencement of the change increases. Finally, it is to be noted that the speed of conversion is considerably diminished by repeated fusion and solidification; if, however, several weeks be allowed to elapse between two experiments, the velocity of conversion will be found to have increased, although it never again attains the same high value as with 'new' sulphur, i. e. sulphur which has been repeatedly crystallized from carbon bisulphide, then pulverized and freed from any adhering solvent by warming at a temperature below 90° . It must therefore be concluded, that, on heating molten sulphur, some molecular change is caused which influences the properties of the substance even after solidification has occurred.

Another excellent example of physical isomerism, or more particularly of polymorphism, is afforded by ammonium nitrate. Frankenheim observed that this substance crystallizes in rhombohedra at high temperatures, whilst under ordinary conditions it assumes an orthorhombic form. According to Lehmann's researches ammonium nitrate is tetramorphous. Its melting point is about 168° , but is considerably influenced by the presence of a little moisture, from which it is almost impossible to purify the substance. As the molten mass begins to solidify, eight-rayed skeletal crystals are deposited; these are seen to be isotropic in polarized light, and consequently

belong to the cubic system. As the cooling continues, a sudden change occurs at 127° , and the crystals become doubly refracting ; those which are still in the liquid part, change their form and at the same time increase considerably in size, owing to the new modification being less soluble than the cubic one. The new crystals are found to be rhombohedra by observation of their shapes, their forms of growth, and their optical properties ; this, therefore, is Frankenheim's rhombohedral modification. On allowing the temperature of the magma to fall to 87° , acicular orthorhombic crystals separate and develop themselves in regular positions about the rhombohedral individuals already present. The orthorhombic crystals are elongated along the vertical axis, and usually arrange themselves so that this easily recognized axis coincides with one of the lateral axes of a hexagonal individual, whilst the brachy- or the macro-axis runs parallel to the principal axis of the latter. Not infrequently also the vertical axis of the orthorhombic crystal lies perpendicular to a lateral axis of the rhombohedron ; the mutual positions assumed by the axes of the two modifications are, however, always perfectly regular, and not merely fortuitous. The needle-shaped orthorhombic crystals consist of an approximately right-angled prism and a dome form ; a pyramid form is also sometimes present. This modification is not identical with that in which ammonium nitrate is deposited from its aqueous solution, although this form is also an orthorhombic one. On heating ammonium nitrate the modifications change into each other in the reverse order. At 36° the ordinary orthorhombic form changes into the second orthorhombic form which may be recognized by the approximately right-angled prism ; at 87° the rhombohedral modification appears, and at 127° the cubic modification is formed. The mass finally melts at 168° .

Further, each of these changes is accompanied by an absorption of heat.

Potassium nitrate behaves similarly to the isomorphous ammonium nitrate, but in the former case no cubic modification has yet been observed.

A large number of physically isomeric substances have been closely examined microscopically by Lehmann, whose results are recorded in numerous papers¹. Since the crystallographic examination of the individual modifications can be only incompletely carried out by microscopic methods, this work has not the crystallographic importance which it would otherwise possess. Lehmann's work is, however, of the greatest importance to chemistry, since it makes possible a method of microscopic analysis; by the aid of this, substances of indefinite melting point, which it is difficult or impossible to obtain in measurable crystals, can be identified or recognized with ease and certainty. Such investigations are therefore worthy of all attention; special mention may also be made of a work by Haushofer², which shows to what great importance the micro-crystallographic examination of substances has already attained in practical chemical work, and more particularly in analytical investigations.

¹ *Zeitsch. f. Kryst* i. 97, 626; iv. 609; v. 472; vi. 48, 580; viii. 433, 529; x. 1, 321; xii. 377.

² *Mikroskopische Reactionen*, Braunschweig, 1883.

CHAPTER XXIII.

THE NATURE OF PHYSICAL ISOMERISM.

It has been already mentioned that physical isomerism is probably due to the different kinds of grouping of the chemical molecules which make up the physical molecules or structural units. Lehmann has, however, attempted to institute a further classification ¹ by distinguishing between physically 'polymeric' and physically 'metameric' substances.

Amongst the former, the individual modifications of a substance differ in the *numbers* of chemical molecules which unite to build up one physical molecule; the latter only differ in the *arrangement* of the chemical molecules within the physical molecule. Physically polymeric substances are supposed to be those in which the change of one into the other only proceeds in one direction; amongst physically metameric substances, the first (labile) modification can be converted into the second (stable) form, whilst the second modification cannot be directly converted into the first. Ostwald ², however, considers that this distinction is scarcely possessed of much importance, since the different behaviour of the two classes of substances can be very readily explained from their melting points. There is, in general, for each physically isomeric modification of a substance a definite range of temperature within which

¹ *Loc. cit.*

² *Lehrbuch der allgemeinen Chemie*, 2nd ed. p. 948.

it is stable ; it is easily seen that the possibility of inter-conversion of the several modifications in one or both directions must be determined by whether the melting point lies within or without this range of temperature. If the melting point lies above the thermometric range of stability for any two modifications, the inter-conversion of these will be possible in both directions. Should the melting point, on the other hand, lie within these limits, the sudden cooling of the molten and overheated substance will give rise to the modification stable at the higher temperature ; although this may persist for some time at the ordinary temperature, there will always be a tendency for it to revert to the modification which is stable at the lower temperature.

The experimental evidence adduced by Lehmann is thus not sufficient to definitely establish the distinction between physically polymeric and metameric substances ; nevertheless, much may be said, *a priori*, in favour of such a classification. The distinction can only be established when methods for determining the size of the physical molecules or structural units are discovered. Several suggestions as to the possibility of this are made by Groth in his Munich inaugural address¹, to which the reader is referred.

The fact that the conversion of one physically isomeric modification of a substance into another, as in the case of sulphur, is accompanied by a considerable evolution or absorption of heat, renders it at least probable that the two states differ in the number of chemical molecules which form one physical molecule or structural unit ; the principal argument in favour of this, is that the analogous inter-conversion of the two gaseous forms of sulphur is also accompanied by an absorption or evolution of heat. The size of the physical molecules, i. e. the smallest freely

¹ *Über die Molekularbeschaffenheit der Krystalle*, Munich, 1888.

moving particles, can be exactly determined in the case of the gaseous modifications, whilst the same information respecting solid bodies can only be deduced from speculations of questionable legitimacy, or be based on conclusions drawn from analogy.

In the discussion of problems such as these the results of thermochemical investigations are of the greatest importance. If, for example, the quantity of heat corresponding to the combination of two chemical molecules were known, it would be possible to arrive at some general conclusions respecting the size of the physical molecules or structural units of the various modifications of a substance from determinations of the heats of solution of the latter. At present the above heat equivalent is not known in any particular case; without the knowledge of this, however, some information may be obtained by comparison of the heats of solution, although the different crystalline forms or crystalline structures certainly correspond to different heat equivalents.

Another possible method of determining the relative molecular magnitudes of physically isomeric substances seems to lie in a purely chemical province. Tschermak has shown that the minerals of the pyroxene group can be referred to a silicate of the composition $\text{CaMgSi}_2\text{O}_6$; for a certain quantity of silicic acid this contains exactly one atom of calcium and one atom of magnesium, its molecule must therefore contain at least two divalent metallic atoms. The pyroxenes are, however, isodimorphous with the amphiboles, and have as their basis a silicate of similar constitution, but which contains only one atom of calcium for every three of magnesium. The molecules of this class of minerals must therefore contain at least four bivalent metallic atoms and, using the simplest possible chemical formulæ, contain twice as many atoms as those of the

pyroxenes. It is, however, pretty well established that the structural units of the two groups of minerals are of corresponding sizes, that is to say, the smallest individual particles taking part in the structure of the crystal contain twice as many atoms or chemical molecules respectively in the case of the pyroxenes as in that of the amphiboles. Using Lehmann's method of description, this would be termed a case of physical polymerism. The question now at once arises:—What relation do the members of these groups bear to each other? Do they afford an example of physical isomerism, or are they isomorphous amongst themselves? The generally received assumption, that one and the same physical molecule or structural unit can only assume one single crystalline form, obviously favours the first of these views¹; leaving this hypothesis out of consideration, however, the differences between the individual members of these groups of minerals may be attributed to their crystalline structures, since different point systems are known² which explain the transition between the several crystalline systems.

It is important to observe that those kinds of crystals which externally seem to possess a higher degree of symmetry than is actually the case, frequently have a lamellar structure; the optical anomalies often exhibited by apparently cubic, hexagonal, or tetragonal substances are closely connected with this. The latter phenomena are attributed to the existence either of internal tension or of twinning in the crystal; the first view has been supported principally by C. Klein, the second by Mallard. The attempts to explain these phenomena on the ground of internal tension have no bearing on the question of dimorphism and therefore will not be further discussed here; the explanation of optical anomalies as the result of twinning, however,

¹ Cf. Brügger, *Zeitsch. f. Kryst.* xii. 500.

² Cf. pp. 105, 165.

closely affects the question under consideration. The hypothesis of twinning would receive considerable support, if, in any individual case, crystals could be shown to have a lamellar composite structure; the mica combinations of von Reusch are of the greatest importance in connexion with this, since, by the regular piling up of thin plates of biaxial mica, the optical characters of a uniaxial crystal can be closely imitated.

If the last-mentioned view be the correct one, then, as Groth pointed out in his address, the dimorphism of those substances whose modifications possess crystalline forms which are very closely inter-related, but belong to different systems, may be explained by the assumption that, in the modification of least symmetry, the structural units are arranged in parallel positions, whilst in the modification of higher symmetry the elements in the different alternating layers have acquired different orientations, owing to the operation of a kind of twinning. Such a method of considering the question is yet further supported by the fact that the point systems (Sohncke's) of high symmetry may be often derived by combining those of lower symmetry; point systems of this kind are all characterized by the fact that their structural units are not arranged in parallel positions. There is thus a perfect agreement between Mallard's views respecting these optical anomalies and Sohncke's theory. The two have hitherto stood somewhat apart, because Mallard's considerations were based upon Bravais' theory, which, as mentioned above, deals only with parallel positions of the structural units. Mallard recognizes only the space-lattices as forms of structure, whilst Sohncke's point systems include not only these, but also forms of structure derived from differently orientated and interpenetrating space-lattices. The circumstance that Mallard was enabled to simplify Bravais' theory in the direction of

Sohncke's point-system theory by a somewhat roundabout and experimental method, should be distinctly recognized, since the subject was considerably advanced thereby.

The hypothesis of physical metamerism is thus shown to be unnecessary for the explanation of the foregoing facts; the second kind of dimorphism or isomorphism¹, which exists between the feldspars, the pyroxenes, the amphiboles, the beryllium sulphates, &c., should much rather be referred to differences in crystalline structure.

¹ Mallard attributed both kinds of dimorphism to polymerism; since he only recognized space-lattices as forms of structure, his structural units consist of several Sohncke units.

CHAPTER XXIV.

HISTORICAL SKETCH OF ISOGONISM.

THE discovery of isomorphism was of the greatest importance not only to crystallography, but also to chemistry. In the latter science, as has been already stated, the first effect of the recognition of isomorphism was seen in its application to the determination of many of the atomic weights; the new discovery, however, also rendered valuable service in other directions. Thus, the composition of selenic acid was first correctly established on the ground of the isomorphism of the selenates with the corresponding sulphates; similarly, from observation of the similarity in crystalline form existing between the permanganates and perchlorates, Mitscherlich discovered the nature of the then unknown permanganic acid. Rammelsberg, in his investigation of the vanadates, also derived considerable assistance from the discovery of the analogy existing between their crystallographic constants and those of the phosphates.

As, however, our knowledge of organic chemistry increased, attempts were made to trace in that branch of the science the regularities already observed in inorganic chemistry; these consisted, partly in a closer investigation of isomorphism, but, to a far greater extent, in the endeavour to arrive at conclusions as to the then problematic nature of many new compounds by the aid of crystallography.

Foremost in this work were the French chemists Laurent, Nicklès, de la Provostaye and Pasteur, who all made numerous crystallographic examinations of organic substances previous to 1850.

Laurent principally investigated the halogen derivatives and addition compounds of naphthalene, and also the salts of some aliphatic acids; his measurements led him to the view, that the divisions between the individual crystalline systems should be broken down. He therefore concluded that identity of crystalline system was not essential to isomorphism, but that an equality or similarity of certain angles only should exist.

Nicklès worked principally on the salts of the homologous aliphatic acids, but—as did also de la Provostaye—included in the range of his investigations many inorganic compounds, comparing, for instance, the chlorate and perchlorate of potassium. Like his fellow workers, he applied the term isomorphism to a general similarity of angles, thus weakening the limitations imposed by the crystalline systems; he was also led to devise new names, such as hemi-isomorphism, isomeromorphism, hemimorphism, &c., for those cases in which similarity in the angles of chemically analogous or isomeric substances is found only in single zones.

Pasteur also seems to have arrived at similar views to the preceding, although he did not formulate them in so precise a way. During his work on the tartrates he noticed such angular similarities; he contented himself, however, with the general remark that certain similarities in the external form of the salts could not be overlooked, in spite of the different proportions of water present. He also stated that no generally applicable law governing these phenomena could be enunciated.

Speaking generally, the above workers arrived at no

very satisfactory conclusions; and the cherished expectations with regard to the clearing up of many obscure questions in organic chemistry were not fulfilled. The investigations also fell somewhat into discredit, owing to the detection by Kopp (d. 1892)¹ of numerous errors in statements of fact. It is therefore quite easy to understand why most chemists shrank from further crystallographic investigations, especially when isomorphism had meanwhile lost considerably in importance in the determination of atomic weights. Only a few prominent investigators worked on in the old direction; amongst these may be especially mentioned Rammelsberg and Marignac (d. 1894), whose numerous investigations considerably increased our knowledge of crystallographic chemistry, and who, without intermission, pushed on the development of the science.

It is noteworthy, that the first attempts to extend the idea of isomorphism, so as to include cases in which analogy exists between substances crystallizing in different systems, originated amongst the chemists, and were hotly opposed by the physicists; Frankenheim was thus one of the foremost in this opposition. The mineralogists, on the other hand, divided themselves between the two parties; Delafosse recognized two kinds of isomorphism, that discovered by Mitscherlich, in which identity of crystalline system is a first essential, and that observed by Laurent, which is not subject to this limitation; other workers, as Zehme, &c., did not make so sharp a distinction. Rammelsberg early gave his allegiance to the latter party; he considered, for instance, that the various crystalline systems are mere artificial divisions which are frequently broken down and which constitute no hindrance to the expression of isomorphism.

A brief account may be given here of the opinions

¹ *Jahresber. f. Chem.* 1849, 19.

held by Scheerer, although they have no real theoretical value, owing to their being based on erroneous assumptions. As is well known, there is a class of crystalline minerals which have in course of time undergone a chemical change without a corresponding alteration in crystalline form taking place (pseudomorphs). Scheerer, however, overlooked this circumstance, and attributed the same crystalline form to both the original substance and its alteration product; he thereby arrived at strange views, such as that serpentine and olivine are isomorphous. He concluded from his observations that the groups MgO , K_2O and $3\text{H}_2\text{O}$, and also 2SiO_2 and $3\text{Al}_2\text{O}_3$, are isomorphous. It is evident that these considerations have only an historical interest at the present time. Sella¹ and Hjortdahl² must yet be noticed amongst the workers who contributed to the extension and firm establishment of the laws of isomorphism or isogonism. Sella was of opinion that the problems under discussion could be best solved by a systematic investigation of as many chemical compounds as possible; he therefore avoided making hasty generalizations from the results of a small number of observations. Hjortdahl confined his attention principally to homologous series of organic compounds. He found a partial similarity of angles in many cases, and therefore drew conclusions similar to those of Laurent, viz. that a partial isomorphism must be supposed to exist.

About twenty-five years ago a considerable change in crystallographic chemistry was brought about by the work of Groth. Until that time all investigators concerned in the examination of organic compounds had striven to apply to them the idea of isomorphism, which had been so fruitful in organic chemistry. Groth attacked the

¹ *Mem. R. Acc. di Torino* (2^a) xvii. 337, and xx. 355.

² *Journ. f. prakt. Chem.* xciv. 286.

problem from another and more general standpoint, asking the question which had been so frequently put with success in many analogous but purely chemical problems :—What alteration occurs in the crystalline form of a chemical compound of which numerous derivatives exist, when certain atoms or groups of atoms are replaced by others? His first investigation was confined to benzene and its derivatives. This hydrocarbon has the composition C_6H_6 , and, since each of the six hydrogen atoms may be replaced by many others, a very large number of derivatives may be prepared. These are mostly solid substances, and are consequently adapted to crystallographic examination. A close comparison of the crystalline form of the derivatives with those of the parent substance, revealed many relations similar to those which Laurent and others had previously discovered.

The crystalline system is sometimes altered by the substitution, sometimes not; but certain individual zones on the crystals invariably show a striking similarity in their angles. In order to better exhibit these relations, Groth arranged the crystals of the substances concerned, in such a way that the corresponding zones should be parallel to one and the same crystallographic axis. The changes in the zones, caused by the substitution, would be thus rendered evident in the most simple manner by a lengthening or shortening of the axis. Relations of this kind were described as ‘morphotropic.’ Groth’s method of consideration certainly offers no explanation of the facts of ‘morphotropy’ as a whole; it arranges them, however, in the simplest and most natural manner, without demanding the recognition of any definite hypothesis at the outset. It will be shown later, that all the changes in crystalline form consequent on substitution cannot be conveniently expressed by the axial ratios; the comparison of crystalline forms is, however, by no means subject to this limitation.

A better insight into the relations between crystalline form and chemical composition can be expected to result only from a more perfect knowledge of crystalline structure. Meanwhile, Groth's method of considering the matter affords the best possible means of reviewing and co-ordinating the experimental data. The study of morphotropy is already so far advanced as to be of some service to pure chemistry and will consequently be specially considered in the following chapter.

CHAPTER XXV.

MORPHOTROPY.

IN accordance with modern chemical views, the greater number of chemical substances are considered as derived from a few typical compounds by the replacement of individual atoms or groups of atoms by others; the chemical character of the compound is naturally more or less changed by such a substitution. What alteration occurs in the crystalline form, as the result of such a replacement? An atom or atomic group is credited with a greater or less morphotropic value according as its entrance into a molecule is attended by a great or small alteration in the crystalline form; the general conclusion arrived at is that the less the chemical character of a compound is changed by the substitution, so much the smaller is the alteration which occurs in the crystalline form. Since now different elements or groups of elements are known which possess completely analogous chemical characters, it is easy to understand that cases may occur in which similar changes in crystalline form result from different substitutions in one original compound. Thus, the two normal salts obtained by replacing the two hydrogen atoms in sulphuric acid, first by lead, then by barium, possess almost identical crystalline forms; they are isomorphous. When considered in this way, isomorphism appears merely as a special case of morphotropy.

Elements or atomic groups which replace each other isomorphously, may be conveniently described as 'isomorphotropic.' The change in crystalline form consequent on substitution by a certain atom, is by no means a constant one; it depends principally on the nature of the compound in which the replacement occurs. The general principle may be stated, however, that substitution in a large molecule causes less change in the crystalline form than substitution in a small one. In accordance with this, it is sometimes observed that certain elements behave as isomorphous in some compounds, but not in others.

A brief classification is given below of those elements or atomic groups which are isomorphotropic; i. e. which, when replacing each other in any compound, do not, as a rule, cause any radical change in the crystalline form.

(1) Chlorine, bromine, iodine, fluorine, and cyanogen in the so-called haloid salts; chlorine and bromine behave like manganese in oxygen compounds.

(2) Sulphur and selenium. In many compounds, as for instance the metallic minerals, these elements are isomorphous with arsenic and antimony, and in others, such as the acids H_2RO_4 , with chromium, manganese, and tellurium.

(3) Arsenic, antimony, and bismuth are isomorphotropic in many sulphur compounds and isomorphous in the free state. In the acids, arsenic can be replaced by phosphorus, and in organic bases by nitrogen.

(4) Potassium, ammonium, caesium, rubidium, and sodium are isomorphotropic in most of their compounds. The most frequent exceptions are observed in the case of sodium; not infrequently also, this element can replace silver or lithium. The thallium salts often correspond in crystalline form to the salts of the alkali metals.

(5) Barium, strontium, lead, and calcium replace each

other isomorphously in anhydrous compounds. The salts which contain water of crystallization, however, always contain it in different proportions; the crystalline form therefore changes. In some few salts barium is isomorphotropic with copper, and calcium with magnesium.

(6) Magnesium, zinc, beryllium, cadmium, iron, nickel, cobalt, and manganese behave as isomorphotropic in most compounds, that is, so long as the latter metals are bivalent.

(7) Iron and manganese, on the other hand, are replaceable by aluminium and chromium in most cases in which they are trivalent.

(8) Copper and silver are isomorphotropic in most of their proto-compounds.

(9) The platinum metals — platinum, palladium, iridium, osmium, ruthenium, and rhodium—are usually isomorphotropic or isodimorphous.

(10) Silicon, germanium, zirconium, titanium, and tin can replace each other in the fluosilicates.

Only those elements or radicles which replace each other isomorphously in most of their compounds are classified together in the above list. Much larger numbers of often very different radicles can indeed replace each other without essentially changing the crystalline form in more complex molecules; the condition then, however, always holds, that the chemical character of the compound suffers but slight change. Thus, for example, the cubic form of the alums remains absolutely the same, when a large number of organic ammonium bases are substituted for the alkali metal or the ammonium. Ammonium platino-chloride shows a similar behaviour; this substance crystallizes in the cubic system, and on replacing the hydrogen atoms of the ammonium, one by one, by methyl groups, Topsoë found the crystalline form to be unaffected.

Substitution by ethyl groups, however, changes the crystalline system, although a great similarity in angular dimensions is still observed, as is shown by the following table¹:—

Composition.	System.	$\begin{Bmatrix} \text{11}\bar{1} : \text{1}\bar{1}\bar{1} \\ \text{111} : \text{1}\bar{1}\bar{1} \end{Bmatrix}$	$\text{111} : \bar{1}\text{11}$	$\text{111} : \text{1}\bar{1}\bar{1}$
$2\text{NH}_4\text{Cl}, \text{PtCl}_4$.	Cubic	$70^\circ 32'$	$70^\circ 32'$	$70^\circ 32'$
$2\text{NMe}_4\text{Cl}, \text{PtCl}_4$.	Cubic	$70^\circ 32'$	$70^\circ 32'$	$70^\circ 32'$
$2\text{NMe}_2\text{Et}_2\text{Cl}, \text{PtCl}_4$	Tetragonal	$72^\circ 43'$	$72^\circ 43'$	$66^\circ 4'$
$2\text{NMeEt}_3\text{Cl}, \text{PtCl}_4$	Tetragonal	$70^\circ 49'$	$70^\circ 49'$	$69^\circ 57'$
$2\text{NEt}_4\text{Cl}, \text{PtCl}_4$.	Monosymmetric	$\begin{Bmatrix} 68^\circ 42' \\ 67^\circ 59' \end{Bmatrix}$	$69^\circ 19'$	$73^\circ 52'$

Generally speaking, substitution alters the crystalline form of a compound in two ways,—the degree of symmetry may be increased or diminished, on the one hand, or, on the other, the axes may be lengthened or shortened.

If only one or a few of the equivalent atoms in a compound are replaced by others, the crystalline system generally changes; and usually in such a way that the new system possesses less symmetry than the old. If, however, most or all of the equivalent atoms are displaced by others, the new derivative ordinarily crystallizes in the same system as the parent substance. The effect of substitution is, however, always greatly influenced by the chemical nature of the compound in which substitution occurs; as already observed, the effect is, in general, less in molecules containing many atoms than in those containing only a few.

The influence of substitution on the crystalline form of

¹ Groth, *Zeitsch. f. Kryst.* viii. 284.

benzene and its derivatives has been the most completely investigated; these substances deserve the closer attention inasmuch as Groth discovered the law of morphotropy by their study. Benzene crystallizes in the orthorhombic system; on replacing one or several of its six equivalent hydrogen atoms by an OH- or NO₂- group, the crystalline system usually remains the same; and even when the substitution extends to two or more hydrogen atoms, the symmetry of the crystalline form is not as a rule diminished. The length of only one axis changes considerably, those of the two others remaining practically constant. This is analogous to what occurs in the case of isomorphous compounds; morphotropic substances are, however, sharply distinguished from these by their inability to crystallize together. The following table gives some examples of the kind of changes caused in the crystalline form of benzene on substitution by hydroxy- or nitro-groups; these derivatives are all orthorhombic:—

Substance.	Composition.	Axial Ratios. <i>a</i> : <i>b</i> : <i>c</i> .
Benzene . . .	C ₆ H ₆	0.891 : 1 : 0.799
Phenol . . .	C ₆ H ₅ .OH	Unknown
Resorcinol . . .	C ₆ H ₄ (OH) ₂ . 1 : 3	0.910 : 1 : 0.540
Pyrocatechol . .	C ₆ H ₄ (OH) ₂ . 1 : 2	Unknown
Nitrophenol . .	C ₆ H ₅ .OH.NO ₂ . 1 : 2	0.873 : 1 : (0.60 ?)
Dinitrophenol . .	C ₆ H ₃ .OH.(NO ₂) ₂ . 1 : 2 : 4	0.933 : 1 : 0.753
Trinitrophenol . .	C ₆ H ₃ .OH(NO ₂) ₃ . 1 : 2 : 4 : 6	0.937 : 1 : 0.974
Dinitrobenzene . .	C ₆ H ₄ (NO ₂) ₂ . 1 : 3	0.9430 : 1 : 0.5384
Trinitrobenzene . .	C ₆ H ₃ (NO ₂) ₃ . 1 : 3 : 5	0.9540 : 1 : 0.733
Picric acid . . .	C ₆ H ₂ (NO ₂) ₃ OH . 1 : 3 : 5 : 6	0.937 : 1 : 0.974

The two following compounds are monosymmetric, thus forming exceptions to the general rule:—

Substance.	Axial Ratios $a : b : c.$	$\beta.$
Orthodinitrobenzene .	0.6112 : 1 : 0.5735	67° 53'
Paranitrophenol .	$\left\{ \begin{array}{l} 0.6625 : 1 : 0.6849 \\ 0.6796 : 1 : 0.3445 \end{array} \right.$	$\left\{ \begin{array}{l} 76^{\circ} 37' \\ 79^{\circ} 6' \end{array} \right.$

On introducing a chlorine or bromine atom, or a methyl or ethyl group into the benzene ring, the substitution affects not only one zone, but usually causes a degradation of the crystalline symmetry; the morphotropic powers of these radicles are consequently greater than those of nitro- and hydroxy-groups. The derivatives thus obtained mostly crystallize in the monosymmetric system; and, since the axial lengths are considerably altered by the obliquity of the axes, the effect of the substitution is not always well and simply expressed by the axial ratios. The following table therefore gives the angles directly measured:—

Substance.	System.	Angle.
Benzene	Orthorhombic	110 : 110 = 96° 30'
Dichlorobenzene .	Monosymmetric	110 : 110 = 98° 40'
Tetrachlorobenzene .	„	110 : 110 = 96° 17'
Dibromonitrophenol .	„	120 : 120 = 93° 45'
Nitrotoluene . . .	Orthorhombic	110 : 110 = 95° 16'
Dinitrotoluene . .	Monosymmetric	110 : 110 = 98° 51'
Nitrotoluidine . .	„	110 : 110 = 95° 58'
Nitrocumene . . .	„	110 : 110 = 95° 15'

It is important to notice that the morphotropic effect of a substitution is also dependent on the orientation of the derivative obtained. Three isomerides of each of the di-substitution derivatives of benzene are possible, and they differ in crystalline form as well as in chemical properties.

The geometrical constants of the three dinitrobenzenes are given below :—

Substance.	System.	Crystallographic Constants.
Orthodinitrobenzene .	Monosymmetric	$0.6112 : 1 : 0.5735$ $\beta = 67^{\circ} 53'$
Metadinitrobenzene .	Orthorhombic	$0.5302 : 1 : 0.2855$
Paradinitrobenzene .	Monosymmetric	$2.0383 : 1 : 1.0432$ $\beta = 87^{\circ} 42'$

The crystallographic properties of the ortho-, meta-, and para-compounds of the aromatic series are not directly comparable with each other; in order to show their inter-relation, it is better to compare them with the parent substance. The crystalline dinitrobenzenes cannot be compared with mononitrobenzene, since the latter is a liquid; and on comparing their crystalline forms with that of benzene it is perhaps hardly surprising that a relation is only observed in one case, i. e. that of metadinitrobenzene. The prism form cutting the clino-axis of the latter substance at half its length has a somewhat similar angle ($93^{\circ} 22'$) to the primary prism on crystalline benzene ($96^{\circ} 30'$). In other cases in which complete series of substitution-products can be obtained and measured, the crystallographic relations can be traced still further; conclusions respecting the constitution of substitution-products can be sometimes deduced in this way.

Thus, three isomeric trinitrobenzenes are possible having the orientations $1 : 2 : 3$, $1 : 3 : 4$, and $1 : 3 : 5^1$; only two of these are known at present and only the first has been examined crystallographically. This is obtained by nitrating metadinitrobenzene; and since all three isomerides might be formed in this operation, the constitution

¹ Friedländer, *Zeitsch. f. Kryst.* iii. 168.

of the one actually obtained is not demonstrated. It crystallizes in the orthorhombic system and has the axial ratios:—

$$a : b : c = 0.9540 : 1 : 0.7330.$$

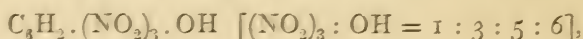
These numbers exhibit a connexion with the axial ratios of metadinitrobenzene. This is best seen by comparing the prism upon half the macro-axis with the primary prism, and interchanging the axes a and b ; the constants then become:—

$$a : b : c = 0.9430 : 1 : 0.5384.$$

The ratio $a : b$ is almost the same in the two cases; the prism angles, however, show the relation at once:—

Metadinitrobenzene . . .	93° 22'
Trinitrobenzene . . .	92° 42'.

No morphotropic relations can be traced between this trinitrobenzene and ortho- or para-dinitrobenzene; the trinitro-derivative should consequently not be an ortho- or para-compound, but might be a dimeta- or 1 : 3 : 5-derivative. Such a conclusion is confirmed by further crystallographic evidence; picric acid has the constitution



and its axial ratios are

$$a : b : c = 0.937 : 1 : 0.974,$$

whilst those of the trinitrobenzene are

$$a : b : c = 0.9430 : 1 : 0.5384.$$

The very obvious crystallographic relation existing between the two substances implies that the positions of the nitro-groups are the same in both.

Similar relations to the above are observed, to a greater or less extent, with all other substances. It is in general true that the morphotropic power of an atom or atomic group depends:—

- (1) On its chemical properties.
- (2) On the chemical properties and complexity of the substance in which substitution takes place.
- (3) On the position in the molecule at which substitution occurs.
- (4) On the crystalline system and crystalline form of the parent substance.

The observation has been frequently made that the higher the symmetry of the parent substance the less is the change in crystalline form caused by substitution. Thus, the cubic form of ammonium alum is unaffected by the entrance of a methyl group in place of an atom of ammoniacal hydrogen, whilst such a substitution in an orthorhombic or monosymmetric compound would lead to a considerable alteration in crystalline form. If the parent substance contains several equivalent hydrogen atoms, it not infrequently happens that the symmetry of the system is decreased by substitution of one of these atoms; but, as several or all of the hydrogen atoms are replaced, the products again crystallize in the same system as the parent substance. This is well shown by the methyl substitution products of ammonium platinochloride:—

Name.	Composition.	System.
Ammonium platinochloride . . .	$2\text{NH}_4\text{Cl}, \text{PtCl}_4$	Cubic
Methylammonium platinochloride .	$2\text{NMeH}_2\text{Cl}, \text{PtCl}_4$	Hexagonal
Dimethylammonium platinochloride	$2\text{NMe}_2\text{HCl}, \text{PtCl}_4$	Orthorhombic
Trimethylammonium platinochloride	$2\text{NMe}_3\text{HCl}, \text{PtCl}_4$	Cubic
Tetramethylammonium platinochloride	$2\text{NMe}_4\text{Cl}, \text{PtCl}_4$	Cubic

For the further illustration of the law of morphotropy the following table may be given:—

Name.	Composition.	*	Geometrical Constants.
Triethylstannic sulphate	$(\text{SnEt}_3)_2\text{SO}_4$	H	$a : a\sqrt{3} : c =$ 0.5773 : 1 : 0.7307
Potassium sulphate .	K_2SO_4	O	$a : b : c = 0.5727 : 1 : 0.7464$
Thallium sulphate .	Tl_2SO_4	O	$a : b : c = 0.5524 : 1 : 0.7365$
Trimethylstannic sulphate	$(\text{SnMe}_3)_2\text{SO}_4$	O	$a : b : c =$ 2(0.5214) : 1 : 1.1766
Silver sulphate .	Ag_2SO_4	O	$a : b : c = 0.5712 : 1 : 1.2386$
Sodium sulphate .	Na_2SO_4	O	$a : b : c = 0.5918 : 1 : 1.2500$
Amidosulphonic acid .	$\text{NH}_2\text{SO}_3\text{H}$	O	$a : b : c = 0.9948 : 1 : 1.1487$
Potassium amidosulphonate	$\text{NH}_2\text{SO}_3\text{K}$	O	$a : b : c = 0.9944 : 1 : 0.7097$
Picric acid . . .	$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$	O	$a : b : c = 0.937 : 1 : 0.974$
Potassium picrate .	$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OK}$	O	$a : b : c = 0.942 : 1 : 1.352$
Maleic anhydride .	$\text{C}_2\text{H}_2 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{O}$	O	$a : b : c = 0.6408 : 1 : 0.4807$
Succinic anhydride .	$\text{C}_2\text{H}_4 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{O}$	O	$a : b : c = 0.5952 : 1 : 0.4619$
Itaconic anhydride .	$\text{C}_3\text{H}_4 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{O}$	O	$a : b : c = 0.6168 : 1 : 0.4545$
Aniline hydrobromide	$\text{PhNH}_2, \text{HBr}$	O	$a : b : c = 0.7230 : 1 : 0.810$
Ethylaniline hydrobromide	$\text{PhNHEt}, \text{HBr}$	O	$a : b : c = 0.7185 : 1 : 0.8180$
Diethylaniline hydrobromide	$\text{PhNEt}_2, \text{HBr}$	M	$a : b : c = 0.7550 : 1 : 1.1254$ $\beta = 83^\circ 4'$
Quinone . . .	$\text{C}_6\text{H}_4\text{O}_2$	M	$a : b : c = 1.0325 : 1 : 1.710$ $\beta = 79^\circ 0'$
Monochloroquinone .	$\text{C}_6\text{H}_3\text{ClO}_2$	O	$a : b : c = 0.4699 : 1 : 0.7064$
<i>o</i> -Dichloroquinone .	$\text{C}_6\text{H}_2\text{Cl}_2\text{O}_2$	M	$a : b : c = 1.0920 : 1 : 1.8314$ $\beta = 89^\circ 1'$
Naphthalene tetrachloride	$\text{C}_{10}\text{H}_8\text{Cl}_4$	O	$a : b : c = 0.7673 : 1 : 0.7003$
Chloronaphthalene tetrachloride	$\text{C}_{10}\text{H}_7\text{Cl}_5$	O	$a : b : c = 0.7927 : 1 : 0.7469$
Dichloronaphthalene tetrachloride	$\text{C}_{10}\text{H}_6\text{Cl}_6$	O	$a : b : c = 0.7521 : 1 : 1.2350$
Trichloronaphthalene tetrachloride	$\text{C}_{10}\text{H}_5\text{Cl}_7$	O	$a : b : c = 0.7273 : 1 : 1.0225$
Santonin acid . . .	$\text{C}_{15}\text{H}_{20}\text{O}_4$	O	$a : b : c = 2.1844 : 1 : 1.4404$
Methyl santonate . .	$\text{C}_{15}\text{H}_{19}\text{MeO}_4$	O	$a : b : c = 1.9961 : 1 : 1.8521$
Ethyl santonate . .	$\text{C}_{15}\text{H}_{19}\text{EtO}_4$	O	$a : b : c = 2.2145 : 1 : 1.4690$

* In the third column the letter H signifies that the substance is hexagonal, O that it is orthorhombic, and M that it is monosymmetric.

A curious morphotropic relationship was shown by Scacchi and vom Rath to exist between the three minerals whose axial ratios are given in the following table:—

Name.	Crystalline System.	$a : b : c.$	$\beta.$
Chondrodite .	Monosymmetric	1.08630 : 1 : 3.14472	90°
Humite . .	Orthorhombic	1.08021 : 1 : 4.40334	90°
Clinohumite .	Monosymmetric	1.08028 : 1 : 5.65883	90°

The axial ratio $\frac{a}{b}$ is practically the same for the three minerals, and the ratios

$$\frac{c}{5b}, \frac{c}{7b} \text{ and } \frac{c}{9b}$$

in the three cases are respectively identical, as will be seen from the table given below; further, Penfield and Howe¹ have recently shown that the three minerals contain 5, 7, and 9 atoms of magnesium respectively in the molecule.

Mineral.	Composition.	Ratio $b : \frac{c}{n}.$
Chondrodite .	$\text{Mg}_3[\text{Mg}(\text{Fl}, \text{OH})_2(\text{SiO}_4)_2]$	$5b : c = 1 : 0.62894$
Humite . .	$\text{Mg}_5[\text{Mg}(\text{Fl}, \text{OH})_2(\text{SiO}_4)_3]$	$7b : c = 1 : 0.62905$
Clinohumite .	$\text{Mg}_7[\text{Mg}(\text{Fl}, \text{OH})_2(\text{SiO}_4)_4]$	$9b : c = 1 : 0.62876$

An undoubted and intimate connexion therefore exists between the composition of these three minerals and their axial ratios. The ratio

$$a : b : \frac{c}{n},$$

where n is the number of atoms of magnesium in the

¹ *Zeitsch. f. Kryst.* 1894, xxiii. 78.

molecule of the mineral, is a constant for the series. It is of interest to note that fluorine is isomorphous with hydroxyl in this group of minerals.

The foundation is still lacking for a theoretical appreciation of morphotropic phenomena; it is at least difficult to reconcile them with the universally accepted theory that crystals are formed by the regular arrangement of their smallest particles. A step towards a theory of morphotropy might be made, as Groth showed in his inaugural address, by supposing that the structural units or liquid molecules of those substances between which intimate morphotropic relations exist are of the same magnitude. Certainly, this affords no explanation of morphotropy, but it at least shows cause why, in many cases, no crystallographic relation can be traced between substances which are chemically closely related; the explanation being, of course, that their structural units contain different numbers of chemical molecules.

INDEX TO AUTHORS' NAMES.

- | | |
|---|--|
| <p> Appiani, 151.
 Armstrong, 150.
 Arzruni, 134.

 Barlow, 14.
 Baumhauer, 102.
 Becquerel, 79.
 Behrens, 48.
 Bergmann, 4, 10, 15.
 Bernhardi, 83, 90.
 Berthelot, 24.
 Berthier, 74.
 Berthollet, 83.
 Berzelius, 85 et seq.
 Beudant, 15, 82 et seq., 91.
 Biot, 91.
 Boyle, 2, 3.
 Brand, 24.
 Bravais, 13, 14, 165.
 Brochant, 84, 88, 143.
 Brögger, 164.

 Cæsalpinus, 2.
 Carangeot, 5.
 Christiansen, 102.
 Clark, 146.
 Cooke, 24.
 Coppet, 33.
 Credner, 156.
 Curie, 14, 65.

 Dana, 12.
 Daniell, 24.
 Dauber, 81.
 Daubrée, 72, 73.
 Debray, 75.
 Delafosse, 12, 169.
 De l'Isle, 4, 5, 82, 143.
 De la Provostaye, 168.
 Deville, 72, 73, 80. </p> | <p> Dossius, 24.
 Drevermann, 78.
 Dufet, 134 et seq.
 Dumas, 96.

 Ebelmen, 74.
 Erlenmeyer, 30.

 Faraday, 146.
 Federow, 14.
 Fock, 127 et seq.
 Forchhammer, 75.
 Fouqué, 74.
 Frankenheim, 12, 13, 46, 64, 158
 et seq., 169.
 Friedländer, 179.
 Fuchs, 72.
 Fuchs, von, 83, 86.

 Gahn, 4, 10.
 Gay-Lussac, 16, 82.
 Geber, 2.
 Gernez, 157.
 Gessner, 2.
 Gibbs, Willard, 33, 39, 126.
 Graham, 24, 30.
 Groth, 92, 134, 165, 171 et seq.,
 184.
 Gortthus, von, 16.
 Guglielmini, 2 et seq., 9.

 Hauer, von, 16, 41.
 Haushofer, 160.
 Häüy, 5, 6, 10 et seq., 82 et seq.,
 142 et seq.
 Heintz, 75.
 Henry, 24.
 Hjortdahl, 170.
 Hoff, van 't, 26, 139, 140, 149. </p> |
|---|--|

- Homberg, 3.
 Hooke, 9.
 Howe, 183.
 Huygens, 9.
 Jannettaz, 101.
 Jordan, 14.
 Karsten, 41.
 Kipping, 51.
 Klaproth, 143.
 Klein, 131, 164.
 Knop, 48.
 Konowaloff, 107.
 Kopp, 96, 97, 169.
 Kuhlmann, 75.
 Lang, von, 8.
 Laurent, 168 et seq.
 Le Bel, 149.
 Le Blanc, 16, 82.
 Lehmann, 45 et seq., 147 et seq.,
 158 et seq.
 Lemery, 2, 3.
 Lévy, 74.
 Link, 46.
 Linnæus, 4.
 Liveing, 65.
 Macé, 78.
 Mallard, 135 et seq., 164 et seq.
 Manross, 75.
 Marignac, 131, 169.
 Maxwell, 65.
 Menozzi, 151.
 Miller, 24.
 Mitscherlich, 74, 84 et seq., 97,
 144 et seq., 166, 169.
 Muthmann, 97 et seq.
 Neminar, 134.
 Nernst, 142.
 Nicklès, 168.
 Nicol, 24.
 Ostwald, 161.
 Pasteur, 150, 152, 168.
 Penfield, 183.
 Pope, 150, 151.
 Provostaye, de la, 168.
 Rammelsberg, 123, 169.
 Rath, vom, 183.
 Retgers, 123, 138.
 Reusch, von, 183.
 Roozeboom, 107, 120 et seq., 130,
 132, 142.
 Rose, G., 75, 85, 155.
 Rosenbusch, 42.
 Rüdorff, 36, 37, 41.
 Sadebeck, 48.
 Sansoni, 134.
 Scacchi, 153, 183.
 Scheerer, 170.
 Schmidt, 46.
 Schönflies, 14.
 Schott, 75.
 Schrauf, 97.
 Schröder, 97.
 Schuster, 103.
 Seeber, 12.
 Sohncke, 13, 14, 67, 104, 105, 151,
 165, 166.
 Sella, 170.
 Senarmont, 73, 76, 102.
 Sorby, 42.
 Spring, 142.
 Steno, 2, 5.
 Stromeyer, 144.
 Thénard, 143.
 Thomson, 19.
 Thorpe, 31.
 Topsøe, 102, 124, 175.
 Trevor, 37, 41.
 Troost, 72, 80.
 Tschermak, 103, 163.
 Tutton, 93, 99, 103.
 Vater, 156.
 Vauquelin, 84, 143.
 Vogelsang, 42, 46 et seq.
 Watts, 31.
 Weiss, 90.
 Werner, 4.
 Wiedemann, E., 31.
 Wiener, 14.
 Wöhler, 146.
 Wollaston, 12, 90, 91.
 Wulff, 56, 69.
 Wyruboff, 137, 138.
 Zehme, 169.
 Zirkel, 42.

INDEX TO SUBJECTS.

- | | |
|---|---|
| <p>Albumen, 16.
 Allotropy, 146, 147.
 Alloys, 140.
 Alums, 16, 64.
 Ammonium chloride, 17, 63, 72.
 Ammonium ferric chloride, 124.
 Ammonium magnesium phosphate,
 47.
 Ammonium nitrate, 158.
 Ammonium tartrate, 64.
 Amorphous state, 61.
 Anatase, 75.
 Anglesite, 75.
 Anharmonic ratio, 7.
 Anion, 38.
 Antimony, 20.
 Apatite, 75.
 Apophyllite, 77.
 Aragonite, 79, 144, 155.
 Arsenates, 99.
 Arsenic, 72.
 Arsenic acid, 85.
 Arsenic anhydride, 80.
 Arsenious anhydride, 16.
 Artificial crystallization, 68.
 Augite, 74.
 Axes of optical elasticity, 103.
 Axes of thermal conductivity, 101.
 Azurite, 79.</p> <p>Barohydrates, 29.
 Barytes, 75, 77, 78.
 Benzene, 171.
 Beryllium sulphate and selenate,
 124.
 Biaxial substances, 103.
 Bismuth, 20, 80.
 Bismuthite, 73, 74, 77.
 Blende, 72, 73.</p> | <p>Boracite, 75.
 Boyle's law, 25.
 Brownian motion, 49.</p> <p>Cæsium salts, 93.
 Calamine, 81.
 Calcite, 6, 9, 79, 81, 144, 155.
 Calcium carbonate, 46, 80.
 Calomel, 72.
 Camphorsulphonic chlorides, 151.
 Capillary constants, 65.
 Carbonates, orthorhombic, 92, 96.
 Carbonates, rhombohedral, 91, 96.
 Cassiterite, 73, 80.
 Cation, 38.
 Cause of crystallization, 16.
 Celestine, 75.
 Chemical molecules, 161.
 Chemical properties of isomorphous
 substances, 106.
 Cinnabar, 81.
 Cleavage, 4, 10, 67, 100.
 Cobalt chloride, 31.
 Colloids, 16.
 Conductivity, thermal, 101.
 Contact goniometer, 5.
 Convection currents, 57.
 Copper, 20, 73, 81.
 Copper pyrites, 63, 73.
 Corundum, 73, 74.
 Crocoisite, 79.
 Crystal, definition, 7, 9.
 Crystal angles, 2, 4.
 Crystal cultivation, 68.
 Crystal growth, 42, 50.
 Crystal structure, 9.
 Crystallites, 47.
 Crystalloids, 16, 47.
 Cupric chloride, 63.</p> |
|---|---|

- Dendritic growth, 59.
 Devitrification, 61.
 Diamond, 74.
 Diffusion, 36, 52, 57, 141.
 Diffusion currents, 52.
 Dimorphism, 80, 145, 146, 151.
 Dissociation hypothesis, 26.
 Distance ratios, 99.
 Distribution, law of, 142.
 Double salts, 36.
 Double sulphates, 93.

 Efflorescence, 63.
 Elasticity, 8.
 Electrolysis, 81.
 Electrolytes, 27, 38.
 Electrolytic deposition, 55.
 Equipotential surfaces, 51.
 Etched figures, 71, 102.
 Expansion of crystals, thermal, 101.

 Face density, 67.
 Fahlore, 63, 73.
 Felspar, 63, 74.
 Ferrous and copper sulphates, 82.
 Fluostannates, 131.
 Fluotitanates, 131.
 Formation of crystals, 45.
 Freezing point, 19.
 Fundamental form, 10.
 Fusion, 73.

 Gahnite, 73.
 Galena, 72.
 Garnet, 74.
 Gaseous state, 23.
 Geometrical symmetry, 8.
 Globulites, 46.
 Goniometer, 5, 91.
 Graphite, 74.
 Greenockite, 73.

 Halhydration, 30.
 Heat of hydration, 30.
 Heat transference, 20.
 Hemihedrism, 13.
 Hemimorphism, 148, 151.
 Heteromorphism, 147, 151.
 Holohedrism, 13.
 Homogeneous mixed crystals, 133.
 Hydration, heat of, 30.
 Hygrohydrates, 29.

 Ice, 19.
 Impurity, influence of, 64, 84.
 Indices, 7.
 Integrating molecules, 10.
 Internal tension, 59.
 Iodine, 17.
 Ions, 27, 31.
 Iron, 20, 80.
 Iron pyrites, 73.
 Isodimorphism, 123, 153.
 Isogonism, 167.
 Isomerism, chemical, 146.
 Isomerism, physical, 143, 146.
 Isomorphism, 82, 87, 89, 92, 104, 140.
 Isomorphotrophy, 174.

 Labile equilibrium, 108.
 Laws of symmetry, 5, 7.
 Lead, 73, 80, 81.
 Limiting forms, 14, 105.
 Longulites, 47.

 Magnetite, 73, 75.
 Malachite, 79.
 Marble, 80.
 Mass-points, 67.
 Melting point, 19.
 Microcrystals, 42.
 Mimicry in crystals, 153.
 Mineral synthesis, 72 et seq.
 Mixed crystals, 82, 107, 132 et seq.
 Molecular change, 80.
 Molecular volumes, 96.
 Molecular weight of solids, 142.
 Morphotropy, 171 et seq.
 Motion during crystallization, 69.

 Naphthalene, 72.
 Nepheline, 74.

 Olivine, 74.
 Optical activity, 148.
 Optical anomalies, 164.
 Optical antipodes, 149.
 Optical characters of crystals, 102.
 Optical isomerides, 149.
 Organic platinochlorides, 176, 181.
 Osmotic pressure, 24, 108, 141.
 Oxyfluomolybdates, 131.
 Oxyfluoniobates, 131.
 Oxyfluotitanates, 131.

- Paraffin wax, 78.
 Para-tartaric acid, 149.
 Pedetic motion, 49.
 Perowskite, 74.
 Phase rules, 32, 39.
 Phases, 108.
 Phosphates, 85, 99.
 Physical isomerism, 143, 161.
 Physical molecules, 161.
 Physical properties of crystals, 8.
 Picric acid, 48.
 Point-systems, 14, 67, 105, 165.
 Polymerism, 166.
 Polymorphism, 145, 146, 151.
 Polysymmetry, 147.
 Porous diaphragm, use of, 77.
 Potassium and thallium chlorates, 121.
 Potassium cadmium iodide, 39.
 Potassium copper sulphate, 37.
 Potassium oxalate, 64.
 Potassium salts, 93.
 Pseudomorphism, 84.
 Quartz, 73, 77.
 Racemic acid, 149.
 Realgar, 77.
 Red silver ore, 73.
 Re-entrant angles, 43.
 Refractive indices and isomorphism, 103.
 Resistance to fusion, 20.
 Rock crystal, 1.
 Rubidium salts, 93.
 Rutile, 63, 73.
 Scheelite, 75.
 Secondary branches, 53, 62.
 Silicotungstates, 131.
 Silver, 74, 80, 81.
 Simple forms, 64.
 Skeletal growths, 49.
 Slags, 61, 75.
 Sobrerol, 150.
 Sodium ammonium tartrates, 150.
 Sodium chloride, 63.
 Sodium platinochloride, 38.
 Sodium sulphate, 32.
 Solid solutions, 115, 140.
 Solution, 17, 24, 76.
 Solvents, 17, 76.
 Space-lattices, 12, 67, 105, 165.
 Specific gravities, 96.
 Specular iron, 63, 73, 75.
 Sphaerocrystals, 60.
 Spinel, 73, 74.
 Stable equilibrium, 108.
 Stannous chloride, 55.
 Staurolite, 73.
 Stibnite, 73.
 Strontium chloride, 30.
 Structural anomalies, 58.
 Structure of crystals, 9, 11.
 Sublimation, 22, 72.
 Sugar, 25, 69.
 Sulphur, 17, 23, 46, 61, 73, 77, 156.
 Superficial energy, 65.
 Supersaturation, 32, 50, 59.
 Surface energy, 65.
 Symmetry, 5, 7.
 Tartaric acid, 148.
 Tertiary branches, 53.
 Thallium and potassium chlorates, 121.
 Thermal conductivity, 101.
 Thermal expansion, 101.
 Thiosulphates, 127.
 Tin, 55.
 Topic or topical ratios, 99.
 Tridymite, 75.
 Trimorphism, 145, 151.
 Twinning, 62, 165.
 Uniaxial substances, 103.
 Urea, 64.
 Vapour tension, 28.
 Vicarious constituents, 83.
 Viscosity, 59.
 Vivianite, 79.
 Volatilization, 17.
 Volume changes, 20.
 Water of constitution, 30.
 Water of crystallization, 29, 86.
 Water of halhydration, 30.
 Willemite, 73.
 Wulfenite, 75.
 Wurtzite, 72.
 Zones, 7.

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